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BY

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THIRD EDITION

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PREFACE TO THE THIRD EDITION

A number of important and radical changes have been made in this, the third edition of this Textbook of Elementary Qualitative Analysis. The theory, in Part I, has been considerably expanded and the more important and generally accepted modern concepts have been introduced. The sections dealing with the various phases of the fundamental background of equilibrium theory have been arranged, with accompanying review exercises, to provide weekly assignments throughout the semester's work.

Part II deals with the reactions of the cations. Here two important changes have been made. First, under the heading of each cation, the characteristic properties and reactions of the ion have been discussed. This is followed by instructions for carrying out preliminary experiments. Second, procedures for the separation and identifications of ions of the several groups and subgroups have been inserted. These procedures are intended to provide practice in the analysis of known mixtures within the various groups Procedures for the analysis of "unknowns" have accordingly been shifted to a later portion of the book.

Part III, on the reactions of the anions, utilizes a new grouping of anions, based on the systematic anion procedure originally developed by Dobbins and Ljung at the University of North Carolina. The author takes this opportunity of acknowledging the service rendered to anion chemistry by these original investigators. The treatment of the anion portion of this book follows the general plan of presentation used for the cations, in that descriptive material, preliminary experiments and practice analyses are provided.

Systematic analysis is presented in Part IV. The procedures provide instructions for the detection of ions in samples ranging in complexity from simple anion and cation mixtures to the more complicated types of solid salt mixtures. Anion procedures precede cation procedures, thus anticipating a minimum of interference.

The author will be grateful for comments and errors which readers will bring to his notice.

Carl J. Engelder

Pittsburgh, Pennsylvania
December, 1941

PREFACE TO THE FIRST EDITION

This Textbook of Elementary Qualitative Analysis is an outgrowth of mimeographed notes in use in the author's classes during the past five years. In preparing this text the writer has had the following purposes in mind: (1) to present the theoretical principles in a manner easily understood and applied by the beginning student; (2) to outline groups of preliminary experiments which demonstrate the properties of the metallic and non-metallic ions that are of importance in analytical procedures; (3) to simplify the procedures for anion analysis and for systematic analysis; and (4) to supply throughout the text sets of exercises and questions designed to direct the student's efforts toward a better understanding of the subject. The aim has been to train the student in logical, independent thinking rather than to teach him specific details of routine analysis.

The fundamental principles of qualitative analysis and the theory of reactions are given in Part I and later elaborated in the procedures of analysis and applied to specific cases. The theory has been treated from the standpoint of ionization and chemical equilibrium.

Sets of review exercises in the form of questions, problems, and the writing of equations and schemes are placed at suitable intervals throughout the theoretical and experimental portions of the text and have proven a valuable aid to both student and instructor. They should constitute a part of the student's written work and may well serve as a basis for classroom discussion. The sets on cation and anion analysis are particularly helpful in aiding the student to anticipate the procedures of analysis which follow.

The analysis of the cations is taken up in Part II. Here are provided, first, the preliminary experiments which form the basis of the methods of separation and identification, together with such other reactions and properties as are of analytical importance. Equations have been freely given, in order to assist the student in correlating properties and understanding the chemical facts

involved. In each group is included a section devoted to a discussion of the application of theory to analysis. Sets of review exercises following the preliminary work on each group direct the student's efforts towards summarizing the results and anticipating the procedure of analysis. The procedures of analysis are given in detail in paragraph form, the necessary explanations, precautions, and remarks on manipulation being made an integral part of the procedure rather than given in subjoined notes. The diagrammatic schemes following the detailed procedures summarize the essential steps of procedure and are not intended as working guides.

Part III covers the detection of the common anions. The order of testing for the individual anions has been carefully worked out with reference to interfering anions. The anions are divided into four groups with respect to their behavior toward hydrochloric acid, barium chloride-calcium chloride reagent, and acidified silver nitrate reagent. Preliminary experiments are given, followed by the procedures of analysis for each group.

The section on Systematic Analysis, Part IV, is designed especially to train the student in the methods of getting substances into solution by solvent and fusion methods. The use of the solubility table is emphasized. The types of samples provide for extended practice in varied technique.

The writer wishes here to acknowledge the criticisms and suggestions of Dr. E. V. Hjort, the aid rendered by Mr. W. A. Morgan in preparing certain tables, and the cooperation of his assistants and pupils in working out the details in the laboratory and classroom. Other texts on qualitative analysis have been freely consulted for methods and ideas, and whatever has been incorporated from them is here gratefully acknowledged.

CARL J. ENGELDER

University of Pittsburgh
June, 1927

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PART I

FUNDAMENTAL PRINCIPLES

Qualitative chemical analysis deals with the methods and principles involved in determining *what* constituents are present in a given material. A quantitative analysis, on the other hand, will show *how much* of each constituent is present. The qualitative analysis of any given substance must necessarily precede the determination of its quantitative composition.

The methods employed in qualitative analysis consist, in general, of separating the constituents from one another by suitable chemical reactions and then applying appropriate reagents which give distinctive identifying tests for the presence or absence of the constituents sought. The selection of reactions for carrying out the necessary separations and identifying tests is based upon the properties and characteristics of the element concerned; hence, from the experimental side, one must gain a thorough knowledge of the behavior of the common metals and acid radicals, the detection of which is considered in this elementary text. From the theoretical side, to understand how a reaction proceeds and properly to interpret the results, one must consider the laws governing reactions; and, since most of the chemical changes take place in solution, the laws and behavior of solutions become of fundamental importance. Little real intelligent progress can be made unless the theory is understood, properly appreciated and correctly applied.

SOLUTIONS

When a small amount of sugar or sodium chloride is added to water the solid disappears in the liquid, forming a homogeneous mixture which is called a solution. All solids show a tendency to dissolve in liquids, the amount of different solids taken up by a given amount of liquid varying between wide limits. Liquids may also dissolve in solids or in other liquids. Gases, too, show this property of dissolving in liquids and in solids. Thus it is

possible to have solutions consisting of solids, liquids and gases dissolved in liquids, as well as solids, liquids and gases dissolved in solids.

The component that is present in greater amount is referred to as the solvent, and the other component is known as the solute. Thus, in a solution of sugar in water, the sugar is the solute and the water the solvent. Water is the commonest solvent used, and throughout qualitative analysis we deal largely with aqueous solutions. Solid, inorganic substances are the chief solutes, although gases and liquids are the solutes in some cases.

A true solution is one in which the solute is disintegrated down to at least molecular dimensions and uniformly distributed throughout the solvent. We may, however, have uniform distribution of a substance in a liquid in which the dispersed substance consists of aggregates of molecules; colloidal solutions and suspensions are of this type. (Colloidal solutions are more fully discussed on page 73.) Throughout this text, the word solution will be used to designate true solutions, and, in fact, aqueous solutions will be implied thereby.

Limits of Solubility. The extent to which the solute will be taken up by a given amount of solvent under definite specified conditions is a characteristic property of the substance. The amounts of different substances which will dissolve in a definite quantity of water, say 1 liter, vary considerably. A solution is said to be saturated when the dissolved material is in equilibrium with an excess of undissolved solute. Inasmuch as these differences in solubility constitute a most useful means in qualitative analysis of separating one substance from another, we must study solubility relationships and select reactions which will differentiate substances on the basis of their solubilities.

If more than the saturation amount of solid is added to a solvent, the excess will remain as undissolved solid, except in those cases where supersaturated solutions form an unstable condition. An idea of the wide variation in the amounts of different solid solutes required for saturated solutions can be gained by reference to solubility tables. (See page 332.) The solubility of a solid in water increases, as a general rule, with increase in temperature and only slightly with increase in pressure. An important application of the general equilibrium theory involving saturated solutions of difficultly soluble salts is discussed on page 63.

Two liquids may be totally or only partially soluble in each other. Thus water and alcohol mix in all proportions and no limit can be placed on the saturation amount. Carbon tetrachloride is only slightly soluble in water and, if the solubility is exceeded, the excess will remain as a second liquid layer; we speak of these two liquids as being practically immiscible in each other. Chloroform, ether, benzene and many other organic liquids form similar two-liquid layer systems with water.

The amount of a gas which will dissolve in a definite volume of water under existing temperature and pressure conditions, too, is fixed by its saturation quantity, and any excess escapes as free gas. In general, the solubility decreases with rise in temperature and increases with an increase in pressure. Some gases, such as hydrogen sulfide, merely dissolve in water, whereas others, such as sulfur trioxide and ammonia, react with water. The solutions of gases in water, whether or not reaction takes place with the solvent, comprise some of our most important and commonest reagents.

Properties of Aqueous Solutions. Experiment shows that many of the properties of water are altered considerably when dissolved material is present. Thus, pure water freezes at 0° C., boils at 100° C. under 1 atmosphere of pressure and exerts a vapor pressure of a definite magnitude at any specified temperature. But when, for example, sugar or sodium chloride is added to water, the freezing point of the water is lowered, the boiling point is raised and the vapor pressure is lowered, the extent of the change in these properties varying with the quantity and nature of the solute present. The osmotic pressure of the solution, too, increases with increased concentration. These changes in vapor pressure, freezing and boiling points and osmotic pressure are all interrelated and if one is known the others can be calculated. Hence, we shall frequently discuss the effect of various conditions on one or two of these quantities, implying but not mentioning the corresponding changes in the others.

Solutes may be divided into two general classes, electrolytes and non-electrolytes, according to the behavior of their aqueous solutions. Compounds like sugar, glycerol, urea and organic compounds in general, are non-electrolytes. If compounds of this type are dissolved in such amounts that the ratio of the number of solute molecules to the number of water molecules in the solution

is the same for the different solutions, the same freezing-point lowering and the same boiling-point rise will be produced in each case. Thus, one gram-molecular weight (one mole) of any non-volatile non-electrolyte dissolved in 1000 grams of water will lower the freezing point 1.86° C. and raise the boiling point 0.52° C. In such a solution there will be 1000/18.016 = 55.51 moles of water to 1 mole of solute or, since a mole of any substance represents a definite number of molecules (Avogadro's number, 6.031×10^{23}) [This value supplants the previous value of 6.06×10^{23}. Cf. Millikan, *Ann. Physik* (**5**), **32,** 520 (1938).] this solution will contain 55.51 water molecules for each solute molecule. It is to be emphasized that the *ratio* between the number of solvent molecules and solute particles is the important factor in determining the effect of a solute on the freezing and boiling points.

Solutions of non-electrolytes, as the term suggests, are very poor conductors of electricity. Electrolytes, on the other hand, contain bonds that are easily broken by the attraction of the solvent molecules when the compound is dissolved. Solutions of electrolytes readily conduct an electric current and exhibit greater deviations in freezing and boiling points than non-electrolyte solutions of the same molecular concentration, i.e., the same number of moles of solute per 1000 grams of solvent.

The Phenomenon of Ionization. To explain the abnormal behavior of dissolved acids, bases and salts, Arrhenius, in 1885, proposed the theory of ionization. This assumes that, when acids, bases and salts are dissolved in certain liquids, particularly water, the molecules of the solute dissociate or ionize to a greater or less extent into positively and negatively charged particles called ions, those bearing positive charges being called cations and those with negative charges anions. Compounds showing this behavior are called electrolytes. The extent of the dissociation depends upon the nature of the solute, the concentration, the temperature and the solvent. The ions behave as independent units irrespective of the nature of the compound from which they are derived, and when two solutions of electrolytes react they show the behavior only of the constituent ions. The phenomenon of ionization can be indicated as a reversible chemical reaction between the dissolved non-ionized molecules and the cations and anions resulting therefrom.

Before the phenomenon of ionization can be further discussed from the standpoint of modern theory it is necessary to call atten-

tion to the present-day concept of atoms, ions, valence and acids, bases and salts.

Atomic Structure. An atom may be visualized as a miniature solar system. A small, very dense nucleus takes the place of the sun, and a number of electrons, called planetary electrons, move about it after the fashion of planets. Each electron constitutes a negative charge of 1.59×10^{-19} coulomb, a coulomb being the amount of electricity represented by a current of 1 ampere flowing for 1 second. The amount of electricity represented by the electronic charge is commonly referred to as a unit of negative charge; the corresponding quantity of positive electricity constitutes a unit of positive charge. The nucleus, which provides practically all the mass of the atom, is made up of units of positive electricity, together with electrons. In the nucleus the electrons are bound to an equal number of protons, producing neutrons; the excess protons remain as unbound positive charges. The number of unbound protons in the nucleus is the *atomic number* of the element. The total number of planetary electrons in the orbits or shells equals the number of excess protons in the nucleus, thus making the atom, as a whole, electrically neutral.

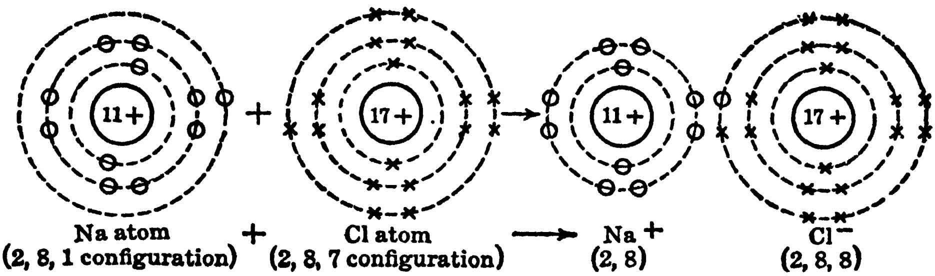
The hydrogen atom consists of 1 proton in the nucleus and 1 electron in the first (or only) shell. The atom of helium contains 2 free protons in the nucleus, and 2 free electrons in the first shell. Lithium has 3 free protons in its nucleus, 2 electrons in the first orbit and 1 in the second, thus giving it the atomic number 3. The sodium atom (atomic number 11) has 2 electrons in its first shell, 8 in the second and 1 in the third. Chlorine (atomic number 17) has 2 electrons in its first orbit, 8 in its second and 7 in its third or outer orbit. Atoms tend to reach a stable configuration of 8 electrons in the outermost shell.

Types of Valence Bonds. Atoms of elements which do not have a stable valence group like that of one of the inert gases have a tendency to attain such a configuration; their chemical properties are then largely determined by the magnitude of the tendency and the manner of attaining the configuration. An atom may secure a stable valence group in either of two general ways:

(1) By *capturing* from one or more atoms enough electrons to make a total of eight in the valence group, or by *losing* to other atoms all the electrons in its own valence group. In the latter case the atom reverts to the next lower stable configuration.

(2) By *sharing* electrons with another atom or with each of several other atoms, each electron so shared being counted in the valence group of each of the two atoms involved in the sharing.

If a stable group is formed, as indicated in (1), by capturing or losing electrons, there is an actual transfer of electrons from one atom to another. This transfer leaves the donor atoms positively charged and gives the acceptor atoms a negative charge, forming cations and anions, respectively. The following equation for the formation of a sodium ion and a chloride ion from an atom of Na and an atom of Cl illustrates such a transfer:



This representation is not to be interpreted too literally. The use of different symbols (circles and crosses) to represent the electrons belonging to sodium and to chlorine does not signify a difference in the nature of the electrons; the purpose is merely to simplify the visualization of the electron transfer. Also, the distribution about the atom is not intended to represent the spatial relations of the electrons to the nucleus in an actual atom; it is simply a means of representing pictorially the successive electronic groups and the number of electrons in each group.

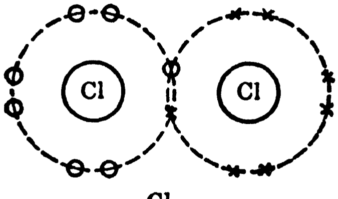
It will be noticed that the single electron in the valence shell of the sodium atom has been transferred to the valence shell of the chlorine atom, forming a sodium ion and a chloride ion, each of which has a stable group of 8 electrons in the outer group. A crystal of NaCl is an aggregate of such ions. It should be emphasized that in compounds of this type *the ions are not formed upon dissolving the material but are already present in the solid compound.* The process of solution involves primarily a separation of the ions, allowing them to act more independently than they can in the crystal.

A valence bond formed in this way is called a polar or ionized bond, and this type of valence is called polar valence, electrovalence

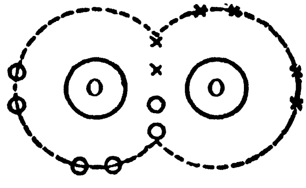
or ionized valence. Each electron transferred gives one unit of polar valence to each of the two atoms concerned in the transfer; the number of such units per atom constitutes the *electrovalence* of the element.

The electropositive elements are those in which the tendency to lose electrons is greater than the tendency to gain electrons in securing a stable group. This is the situation, in general, when the number of electrons in the valence group is less than 4, as it is in most of the metals. If the tendency to gain electrons is greater than the tendency to lose them the element is electronegative. This happens, in general, when there are 6 or 7 electrons in the valence group, as in many of the non-metals. Elements which have 4 or 5 electrons in the valence group, as well as some elements with 3 or 6, or occasionally some other number, show, in general, little tendency either to gain or lose electrons and hence rarely form ionized compounds.

Attainment of a stable group by sharing electrons, as indicated in process (2) (page 6), results in the formation of either covalent or coordinate covalent bonds. Covalent bonds are sometimes called non-polar or homo-polar bonds, and coordinate covalent bonds are sometimes called semi-polar or, frequently, simply coordinate bonds. In this book, for brevity, the term coordinate bond will usually be used. Each *pair* of shared electrons may be considered to constitute a single bond. In a covalent single bond one of the two shared electrons comes from each of the two atoms. This is illustrated by the following diagrams of the chlorine and oxygen molecules. For simplicity, all the electrons except those in the valence group have been omitted in these and all subsequent atomic diagrams.



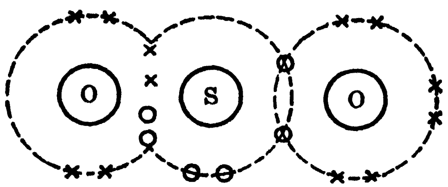
Cl_2
**(Single bond—
two shared electrons)**



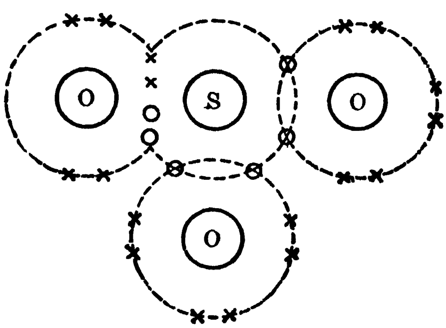
O_2
**(Double bond—
four shared electrons)**

If, instead of each atom supplying one of the two shared electrons, both of the electrons come from the same atom, the result

is a coordinate bond and each pair of electrons so shared constitutes 1 unit of coordinate valence. This is illustrated in the accompanying diagram of SO_2.



The oxygen atom shown on the right in this diagram is joined to the sulfur by a coordinate bond; the one on the left is joined by a covalent double bond. It will be noted that the sulfur atom has another pair of unshared electrons which, presumably, should be able to form a coordinate bond with another oxygen atom. In the SO_3 molecule this additional bond is formed, as is shown in the accompanying diagram.



The diagram of the SO_2 molecule shows that more than one type of valence bond may exist in the same molecule and indicates the difficulty of stating the " valence " of an element or group unless the type of valence concerned is specified. Thus, while sulfur in SO_2 is usually considered to have a " valence " of 4, this valence really consists of a covalence of 2 and a coordinate valence of 1. For convenience, the number 4 may be called the " apparent valence " or " valence number " of sulfur in SO_2; similarly, in SO_3 the apparent valence of the sulfur is 6.

Valence Bonds and Ionization. When a substance containing polar bonds is dissolved in a polar solvent such as water, the polar bonds are broken and the ions move about more or less independently of each other. This is equivalent to saying that compounds having polar bonds are completely ionized in solution, as they are in the solid state. On the other hand, covalent and coordinate bonds usually are not broken in solution; for exceptions, see page 55. This means that atom groups which are held together by shared-electron bonds will usually remain intact and act as units in solution. The fact that the sulfate, phosphate and similar ions act as units in many chemical reactions is explained on this basis.

Although a compound may contain no polar bonds and thus be undissociated or non-ionized in the pure condition, it may be considerably ionized when dissolved in a polar solvent — for example,

water — owing to the attraction of the polar solvent molecules for the atoms of the compound. This type of action will be considered later in some detail in the section dealing with the ionization of electrolytes (page 15).

Variable Valence. Only a few of the elementary features of this interesting subject can be mentioned here. The observant student has already noticed that the number of electrons in the outermost orbit of the atom is not always the same as the number of the group in which the element is found in the Periodic Table. He may also have discovered that, in many cases, if 8 is subtracted from the number of electrons in the next lower orbit and if this difference is added to the number in the outermost orbit the result will be the normal valence group of the element. To illustrate, U has the configuration (4)–18–12–2 and appears in Group VI. If 8 electrons are subtracted from the group containing 12, the difference plus the 2 electrons in the last group totals 6.

The preceding discussion suggests the possibility that electrons may shift into the valence orbit from the orbit next to it, thereby changing the valence of the element. This is essentially what occurs when an element changes from one ionized valence to another. For instance, Fe in the ferrous condition corresponds to the configuration 2–8–14–2. If the 2 valence electrons are lost a ferrous ion, Fe^{++}, results. Fe in the ferric condition corresponds to the configuration 2–8–13–3; loss of the 3 valence electrons in this case results in the formation of a ferric ion, Fe^{+++}. Elements such as K, Ca, Al, etc., have a stable group of 8 electrons in the orbit next to the valence orbit. There is therefore a negligible tendency for electrons to be transferred into the valence group and these elements accordingly exhibit only one valence state.

In passing, it may be pointed out that the shift of electrons from one orbit to another corresponds to the absorption or emission of light or other form of radiant energy. Compounds of metals of variable valence are almost invariably colored, whereas those of constant valence are usually colorless. The phenomenon of color in compounds therefore corresponds to the ease with which electrons shift from one orbit to another in the atoms.

Acids and Bases. *An acid is a substance* (molecule or ion) *having the chemical property of losing a proton to another substance.* Since a proton is the same as a hydrogen ion we can also say that

an acid is a substance that is able to furnish hydrogen ions. This includes all the compounds such as HCl, HNO_3, $HC_2H_3O_2$, etc., which commonly have the term acid included in their names, as well as certain other substances such as HCO_3^-, NH_4^+, H_2O, etc., which usually are not thought of as being acids. Acids are said to be monoprotic, diprotic, triprotic, etc., according to their ability to furnish 1, 2, 3 or more protons per molecule.

A base is a substance (molecule or ion) which has the chemical property of gaining a proton from another substance. In this classification are included such substances as hydroxyl ion, ammonia, acetate ion and the like, since they are able to combine with hydrogen ions as indicated by the equations:

$$OH^- + H^+ \rightarrow H_2O$$

$$NH_3 + H^+ \rightarrow NH_4^+$$

$$C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$$

One of the chief points of difference between the traditional and the modern idea of acids and bases is in the concept of a base. According to the traditional theory a substance is a base if, and only if, it provides hydroxyl ions. The modern theory states that it is not the substance that provides the hydroxyl ion but *the hydroxyl ion itself* that is the base. Thus, NaOH is *not a base* but it *contains* the base, OH^-. Moreover, there are many bases other than the hydroxyl ion, as indicated above. Compounds such as NaOH which furnish a high concentration of hydroxyl ions we call alkalies.

A consideration of the definitions will indicate that every acid is related to some particular base in a definite way. This relationship is indicated by the general equation:

$$\text{acid} \rightleftharpoons \text{base} + H^+ \qquad (1)$$

that is, the substance remaining after the removal of a hydrogen ion from an acid is a base. It will be noticed that the forward reaction provides the definition of an acid, whereas the definition of a base depends on the reverse reaction. An acid and a base that are related in the way indicated by the equation are called a **conjugate pair.** Some examples of conjugate pairs are the follow-

ing, the acid being mentioned first:

H_2O, OH^-	HCl, Cl^-
$HC_2H_3O_2$, $C_2H_3O_2^-$	HCO_3^-, $CO_3^=$
NH_4^+, NH_3	H_2S, HS^-

Our definition states that an acid must be capable of losing a proton *to another substance.* This implies that the proton is transferred from one acid to some proton acceptor and that therefore our simple equation:

$$\text{acid} \rightleftharpoons \text{base} + H^+$$

is incomplete and might better be written:

$$\text{acid} + \text{proton acceptor} \rightleftharpoons \text{base} + (\text{proton acceptor})\cdot H^+ \quad (2)$$

This indicates that in solutions the protons are always present in combination with some other ion or molecule and *never exist in the form of simple hydrogen ions.* The solvent itself frequently functions as a proton acceptor, so the above equation may be rewritten for aqueous solutions in the following form:

$$\text{acid} + H_2O \rightleftharpoons \text{base} + H_2O\cdot H^+ \quad (3)$$

The ion $H_2O\cdot H^+$ or H_3O^+ is called the hydronium or oxonium ion and, owing to the action indicated by the equation, *is present in all aqueous acid solutions.* This is not a "theoretical" statement; the actual existence of H_3O^+ ions is indicated by many types of experimental evidence which, however, cannot be described here.

Consideration of equation (2) leads to a very simple observation. The substance that we have designated as "proton acceptor" agrees with the definition of a base since it accepts a proton from the acid. Also, the H_3O^+ ion satisfies the requirement for an acid since the equation:

$$H_3O^+ \rightleftharpoons H^+ + H_2O$$

describes its nature. The conclusion is that *any acid-base reaction really involves two acids and two bases,* i.e., two conjugate pairs. The most general equation then is of the type:

$$\text{acid}_1 + \text{base}_2 \rightleftharpoons \text{base}_1 + \text{acid}_2$$

where (acid$_1$, base$_1$) and (acid$_2$, base$_2$) are conjugate pairs. For example, the reaction which is usually written as:

$$HCl \rightarrow H^+ + Cl^-$$

is in reality:

$$\underset{(\text{acid}_1)}{HCl} + \underset{(\text{base}_2)}{H_2O} \rightarrow \underset{(\text{base}_1)}{Cl^-} + \underset{(\text{acid}_2)}{H_3O^+}$$

Of course, the solvent is not necessarily included in the equation since some other proton acceptor may be present, as the following equations show:

$$HCl + NH_3 \rightarrow Cl^- + NH_4^+$$

$$H_2PO_4^- + CO_3^= \rightarrow HPO_4^= + HCO_3^-$$

The preceding discussion presents the essential features of the Brönsted-Lowry concept of acid-base reactions. These ideas may easily be extended to non-aqueous solutions and thus are useful in correlating large numbers of otherwise unrelated facts and phenomena. To illustrate, liquid ammonia is slightly ionized as follows:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

a reaction analogous to that for the ionization of water:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Few substances are known which in the solid state contain the H_3O^+ ion; those that do, however, behave as acids in water solution. On the other hand, many compounds are known which contain the NH_4^+ ion and these, when dissolved in liquid ammonia, *behave as acids.* That is to say, NH_4Cl, for instance, is a strong acid in liquid ammonia solution. Likewise, any substance, such as HCl, which can furnish a proton, will act as an acid since by the reaction:

$$HCl + NH_3 \text{ (solvent)} \rightarrow NH_4^+ + Cl^-$$

an ammonium ion is produced. In general, for hydrogen-containing solvents, any substance which in solution gives the same cation as is formed by the ionization of the solvent itself will behave as an acid and any substance that combines with the acid cation will behave as a base. From the ionization equation it is apparent that any substance, such as KNH_2, which supplies the

amide ion, NH_2^-, will act as a base in liquid ammonia; the real base is, of course, not KNH_2 but the amide ion, NH_2^-.

Hydration of Ions. One other point remains to be mentioned. When we consider the hydronium ion, H_3O^+, as a hydrated hydrogen ion it must *not* be supposed that hydration is peculiar to the hydrogen ion. All ions in water solution are hydrated — to an indefinite and unknown extent, to be sure — and might be represented as $Na(H_2O)_x^+$, $Cl(H_2O)_y^-$, and so on. Since the extent of the hydration is unknown and since the inclusion of the water in the formula of the ion contributes little to our knowledge of the properties of the ion, we shall omit it entirely in subsequent discussions. When we look at the formula of an ion, however, we shall remember that the ion *really is hydrated* and that the formula, although it tells the truth, does not tell the *whole* truth.

The situation in the case of the hydronium ion is, however, somewhat different. Owing to its very small size — approximately 1/100,000 of the diameter of an ordinary atom — the proton probably is buried within, or is surrounded by, a single water molecule. This means that, although it is conceivable that the proton may be attached to a number of water molecules, the probability is great that it is associated with only one and, therefore, the degree of hydration is somewhat *less indefinite* than it is for any other ion. Moreover, as mentioned previously, H_3O^+ ions have been definitely identified in some compounds. But now, having justified a belief in the existence of H_3O^+ ions, we shall for simplicity henceforth omit the water from our written formulas, just as we do with the other hydrated ions. The symbol H^+ will suggest, however, that what we are really talking about is the *hydrated proton*, more completely represented by H_3O^+.

Salts. Up to this point we have not even mentioned the term "salt." As a matter of fact, there is no definite place for the word in the Brönsted-Lowry concept, but the convenience and widespread use of the traditional classification make it desirable to retain the term. We may say then somewhat arbitrarily, considering aqueous solutions only, that a salt is a substance which consists of or provides some positive ion other than hydrogen ion and some negative ion other than hydroxyl ion. This is equivalent to the usual definition and will include and exclude the same compounds as the statement that a salt is one product of the neutralization of an acid by a (traditional) base.

It should be pointed out that the class in which a given electrolyte is placed depends in many cases upon the solvent that is being considered. NH_4Cl, for example, is a *salt* in water but an *acid* in liquid ammonia. It is unfortunate in some respects that the universal use of water as a solvent has resulted in the development of a classification applicable in many cases only to water, with the result that far-reaching generalizations applicable to all solvents may be obscured or disregarded.

The Extent of Ionization. If the extent to which different acids, bases and salts ionize is compared for solutions containing equal gram-molecular weights of the solute and at the same temperature, it will be found that this varies considerably with different electrolytes. Electrolytes in moderately dilute solutions, in which the proportion of the ionized to the non-ionized part is large, are strong electrolytes. Examples of strong electrolytes are solutions of HCl, NaOH, NaCl and, as a general rule, most inorganic salts. On the other hand, weak electrolytes are those in which the tendency to ionize in moderately dilute solutions is relatively small, such as solutions of NH_3, $HC_2H_3O_2$, H_2S, H_2CO_3 and water itself.

Table I shows the percentage of ionization of solutions of common acids, bases and salts, each containing 0.1 of the molecular weight of the solute in grams in a liter of solution. Solutions containing this amount of solute are known as 0.1 *M* solutions. Note that for acids the degree or percentage of ionization varies from 92.0 per cent for HCl to 0.01 per cent for HCN, for solutions of equal strength, and that the primary ionization for polybasic acids takes place to a much greater extent than the secondary and tertiary. Note, too, that NaOH is typical of a strong base whereas NH_4OH is a weak base. The behavior of salts depends upon the type and, as a general rule, for such concentrations as are usually employed in laboratory reagents the percentage of ionization is large. A few salts, notably certain salts of mercury, lead acetate, ferric acetate and a few others, are exceptions in that their ionization is abnormally weak.

Ionization and Concentration. The foregoing discussion and Table I have shown that the percentage of ionization differs widely for different electrolytes in solutions of the same concentration. For the same electrolyte the ionization varies with the concentration, if temperature and other factors remain un-

TABLE I

PERCENTAGE IONIZATION OF COMMON ACIDS, BASES AND SALTS IN 0.1 MOLAR SOLUTIONS AT 18° C.

Acid	Ionization Reaction	Per Cent Ionized
Hydrochloric	$HCl \rightleftharpoons H^+ + Cl^-$	92.0
Nitric	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	92.0
Nitrous	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	8.0
Formic	$HCHO_2 \rightleftharpoons H^+ + CHO_2^-$	4.5
Acetic	$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.34
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	0.01
Sulfuric	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	90.0
	$HSO_4^- \rightleftharpoons H^+ + SO_4^{=}$	60.0
Oxalic	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	40.0
	$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{=}$	1.0
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	0.12
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}$	0.0017
Hydrosulfuric	$H_2S \rightleftharpoons H^+ + HS^-$	0.05
	$HS^- \rightleftharpoons H^+ + S^{=}$	0.0001
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	27.0
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{=}$	0.1
	$HPO_4^{=} \rightleftharpoons H^+ + PO_4^{\equiv}$	0.0001
Water	$HOH \rightleftharpoons H^+ + OH^-$	0.0000002
Base		
Sodium hydroxide	$NaOH \rightleftharpoons Na^+ + OH^-$	90.5
Ammonium hydroxide	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.31
Calcium hydroxide	$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$	75.0
Salt	Examples	
Uni-univalent	KCl, $NaNO_3$, NH_4Cl, $NaC_2H_3O_2$	80–85
Uni-bivalent	$CaCl_2$, K_2SO_4, etc.	70–75
Bi-bivalent	$MgSO_4$, $CuSO_4$, etc.	35–45

altered. That is, the more dilute the solution, the greater will be the degree of ionization. If we take, for example, a liter of a 0.1 molar solution of acetic acid, in which the degree of ionization is 1.34 per cent, and dilute it with 9 liters of water, the resulting solution will be only one-tenth as concentrated and if we measure,

by electrical conductivity or other methods, the new degree of ionization, we will find it to be 4.17 per cent at 18° C. Further dilution will result in still greater ionization, until in extremely diluted solutions there is no further increase in ionization. When this point of infinite dilution is reached the solution is 100 per cent ionized.

The variation of the degree of ionization with concentration is shown in Table II for two strong acids, two weak acids, a strong base, NaOH, a weak base, NH_4OH, and a number of salts.

TABLE II

VARIATION OF PERCENTAGE IONIZATION WITH CONCENTRATION AT 18° C.

Electrolyte	Concentration of Electrolyte in Moles per Liter			
	1 *M*	0.1 *M*	0.01 *M*	0.001 *M*
HCl	80.0	92.0	97.2	99.0
HNO_3	85.0	92.0	96.9	99.0
$HCHO_2$ at 25° C.	1.5	4.5	13.4	35.8
$HC_2H_3O_2$	0.4	1.34	4.17	11.7
NaOH	77.0	90.5	93.3	97.1
NH_4OH	0.4	1.31	4.07	11.7
NaCl	74.1	85.2	93.6	97.7
$AgNO_3$		81.4	93.1	97.7
$NaCHO_2$	59.5	85.4	93.1	
$NaC_2H_3O_2$	52.6	77.9	89.4	
NH_4Cl	74.7	85.3	94.0	
K_2SO_4		67.3	83.2	93.7
$MgCl_2$		72.8	85.1	93.9
$MgSO_4$		40.3	59.6	82.3

Note that for the strong acids, for NaOH and for many of the salts, the ionization is nearly complete in 0.001 *M* solution, and that for the weak acids and NH_4OH much greater dilution than shown here will be required to bring about complete ionization. As noted in a previous paragraph (see page 14), a solute is considered a strong electrolyte if the proportion of ions to the non-ionized fraction is large when the total amount of dissolved solute is relatively large. Acetic acid and ammonium hydroxide are not considered strong electrolytes because it is only in extremely dilute solutions that the concentration of ions predominates over the non-ionized molecules.

That increase in ionization is a necessary consequence of increasing the dilution will be shown, on page 56, when the equilibrium relationships in solutions are treated in a quantitative way.

Ionization and Temperature. With an increase in temperature most electrolytes show a decrease in the percentage of ionization. Thus in 0.08 *M* solutions of HCl at 18° C. the percentage ionized is 93.2; at 100° C. it is 89.7. For the same conditions in the case of $HC_2H_3O_2$ the values are 1.5 per cent and 1.17 per cent, respectively. Water is an exception to this rule, the ionization increasing somewhat with rise in temperature.

Effect of Solvent on Ionization. Electrolytes ionize to a greater extent in water than in most other solvents. Water is also the commonest solvent. Other ionizing solvents are liquid ammonia, liquid hydrocyanic acid and liquid sulfur dioxide. The ability of a solvent to bring about ionization is related to its dielectric constant and, in general, the greater the dielectric constant, the better the medium for ionization of the solute to take place. The presence of other dissolved substances also influences the extent of ionization of many solutes.

The Debye-Hückel Theory. We have mentioned previously the abnormal effect of electrolytes on the freezing and boiling points and similar properties of solutions. According to the Arrhenius theory of ionization an ion has the same ability to lower the freezing point (for example) as a non-ionized molecule. Hence, if a molecule divides into 2 ions, 1 gram-molecular weight of the substance in 1000 grams of water should produce a lowering of twice 1.86°, provided the substance is completely ionized. Ordinarily, however, the lowering actually measured is somewhere between 1.86° and 2 × 1.86° for a substance giving 2 ions per molecule, and somewhere between 1.86° and 3 × 1.86° for a substance giving 3 ions per molecule. Arrhenius interpreted this behavior as indicating incomplete dissociation of the solute and calculated the percentage of ionization which would have to occur to account for the experimental results. This explanation seemed to be supported by the observation that when a solution of an electrolyte is diluted the calculated degree of ionization increases until in very dilute solutions it approaches or even reaches 100 per cent.

Since most salts in the solid state consist exclusively of ions it is reasonable to suppose that they would also be completely

ionized in solution. If such is the case some other explanation must be found for the experimental observation that, except in very dilute solution, the freezing-point lowering is less than it would be if each ion had the same effect as a non-ionized molecule. This difficulty exists only for strong electrolytes; weak electrolytes are admittedly incompletely ionized, so the Arrhenius theory is applicable to them.

To account for the behavior of strong electrolytes Debye and Hückel developed mathematically a theory which assumes complete ionization of strong electrolytes in solution. Simply expressed, this theory states that in the immediate neighborhood of any cation there are more anions than cations, and near any anion there are more cations than anions. This may be attributed to the well-known fact that opposite charges attract and like charges repel. A somewhat similar situation exists in salt crystals. In NaCl, for example, each sodium ion is surrounded at equal distances by 6 chloride ions and each chloride ion is likewise surrounded by 6 sodium ions. Consideration of such a crystal may aid in visualizing the situation existing in a solution, but it must be remembered that in the solution the ions are free to move, and the number and distances of the surrounding ions are by no means definite.

The effect of the " cloud " or " atmosphere " of ions surrounding a particular ion is to restrict the motion of the ion in question, for motion of the ion will be opposed by the attraction of the oppositely charged ionic atmosphere. This restriction of motion manifests itself as a decreased activity of the ion, i.e., the ion will have less effect in lowering the freezing point than it would have if its motion were unopposed by oppositely charged ions. As the solution is diluted the distances between the ions become greater, thus decreasing the effect of the ionic atmosphere and allowing the ions to exhibit their full influence on the freezing and boiling points. For very dilute solutions the Debye-Hückel and Arrhenius theories are equivalent as far as we are concerned.

The Concept of Activity. The change produced in the conductivity and related properties when a solution of a strong electrolyte is diluted may be explained in either of two ways: (1) the mobility or freedom of motion of the ions may remain constant but the number may increase, owing to the dissociation of non-ionized

(since there are no non-ionized solute molecules present) but the mobility of the ions may increase, owing to a decreased interference from the ionic atmosphere surrounding each. The first assumption is made in the development of the Arrhenius theory and the second underlies the Debye-Hückel theory. The first condition applies to weak electrolytes and the second to strong electrolytes.

To take into account the experimental fact that strong electrolytes appear to be incompletely ionized, as judged by their effect on vapor pressures, etc., a term called the **activity** or **effective concentration** is introduced. Numerically, the activity of a molecule or ion in a given solution is equal to the concentration that it would have to have to give the observed effect on the vapor pressure *if each molecule or ion had the same effect that it has in a very dilute solution.* The activity is related to the concentration by the expression:

$$\boxed{a = fC}$$

where f is a fraction called the **activity coefficient.**

The activity coefficient is similar in many respects to the degree of ionization used in connection with weak electrolytes. It increases with the dilution and becomes equal to 1 in very dilute solutions. It is decreased by the addition of ions other than the ones under consideration; some results of this behavior will be considered in the discussion of the salt effect (page 72).

The experimental determination of activities and activity coefficients is not easy. Moreover, owing primarily to the difficulty of securing appropriate data, activities do not lend themselves so readily to elementary calculations as do concentrations. It should be realized that even for weak electrolytes and non-electrolytes *activities must be used instead of concentrations if perfect accuracy is desired.* The common failure to do this sacrifices a small amount of accuracy for a considerable gain in simplicity.

REVIEW EXERCISES — SET 1

1. Define a solution. Give examples of the different kinds of solutions with respect to solute and solvent.

2. Differentiate between electrolytes and non-electrolytes; weak and strong electrolytes; acids and bases. What effect has dilution on degree of ionization?

3. From the list of reagents used in the laboratory (see Appendix, page 323) select several examples of each of the following types of solutions: solid-in-liquid; gas-in-liquid; liquid-in-liquid. What other types of solutions exist?

4. A substance which dissolves only to a limited extent may be completely ionized but the solution may not conduct a current as well as a solution of a weak electrolyte such as acetic acid. Is such a slightly soluble compound a strong or a weak electrolyte? Explain.

5. What is the difference in molecular structure between an electrolyte and a non-electrolyte? State whether a compound containing at least one ionized bond must be, may be, or cannot be an electrolyte. Do likewise for compounds containing the other two types of bonds and then consider various combinations of the three types in the same compound.

6. Referring, if necessary, to your general chemistry textbook, state what general conclusions may be drawn as to the solubility in water of each of the following classes of compounds: chlorides, nitrates, sulfates, alkali metal salts, sulfides.

7. Predict how each of the following substances would behave in liquid ammonia solution: $(NH_4)_2SO_4$, KNH_2, H_2O, HCl, KNO_3, Cl^-. If the substance acts as an acid or base write the equation and indicate the conjugate base or acid.

8. What general rule applies to the extent of ionization of electrolytes that ionize in several stages? Illustrate your answer with suitable examples.

9. Explain the Brönsted-Lowry concept of acids and bases. In what respects does it differ from the traditional concept?

10. Describe the essential features of and the differences between the Arrhenius and the Debye-Hückel theories. To what type of solution is each applicable?

REAGENTS

In the laboratory work of qualitative analysis, the experimenter is primarily and continuously engaged in observing and actually applying the effect of reagents on test substances of known and unknown composition. In fact, from the experimental side it may be said that qualitative analysis consists very largely of the correct use of reagents. At the outset, therefore, in the study of this subject, the student must become acquainted with the reagents to be employed, prepare a number of them himself and learn how to carry out the calculations involved in the preparation and use of a wide variety of reagents.

The list of reagents found in the Appendix (page 323) should be examined. Instructions are given on page 23 for the preparation of certain reagent solutions. The preparation of solutions of the samples of known and unknown composition make up an

important part of the laboratory work. It is customary to study first the analytical properties and reactions of the ions separately as detailed under each cation and anion and to follow this by the analysis of mixtures of known composition, designated as " Practice Analyses " before the analysis of samples of unknown composition is undertaken. The test ions are usually supplied in the form of test solutions, the preparation and nature of which are described on the following page.

It is convenient to classify the test substances and reagents under the following heads:

A. Test Substances.
   1. Test solutions.
   2. " Known " mixtures of cation and anion solutions.
   3. " Unknown " samples.

B. Reagents.
   1. Gases, such as H_2S.
   2. Pure liquids, such as the organic solvents ether, chloroform, carbon tetrachloride, etc.
   3. Solid reagents, such as $KClO_3$, NH_4Cl, Na_2CO_3, metals, etc.
   4. Solutions of various kinds made by:
      a. Dissolving gases in water.
      b. Dissolving liquids in water.
      c. Dissolving solids in water.
      d. Diluting " concentrated " reagents.

On the basis of the effect to be produced, the uses to which these reagents are put may be summarized as follows:

1. For dissolving samples, precipitates and residues.
2. For acidifying, neutralizing or rendering a solution alkaline.
3. For precipitating.
4. For oxidizing or reducing.

Methods of Expressing the Concentration of Solutions. The strength of a solution may be expressed in a number of ways; the following types of solutions, with respect to the method, units or system used to designate the concentration, are recognized in analytical chemistry.

1. *Test Solutions.* The so-called test solutions contain the individual ions whose characteristic reactions and properties are

usually studied in the preliminary experiments. A series of cation test solutions, made whenever possible from the nitrates of the metals, and a series of anion test solutions, made from the sodium or potassium salts of the acids, are usually prepared. In these solutions the cation or anion content is kept uniform, each milliliter of solution containing 10 milligrams (0.01 gram) of the ion. These solutions therefore represent one type of concentration measurement. In the Appendix (pages 328–329) will be found a list of cation test solutions and a list of anion test solutions. The preparation of the test solutions involves a simple direct proportion calculation which may be illustrated by the case of the silver-ion test solution.

How much $AgNO_3$ should be weighed out, dissolved in water and diluted to 1 liter, in order that each milliliter will contain 10 milligrams of Ag^+ ion (assuming that all the silver is in the ionic condition)?

Since 1 ml. is to contain 10 milligrams or 0.01 gram, 1 liter will contain 1000×0.01 or 10 grams of silver as Ag^+ ion. It is then a simple matter to calculate the weight of $AgNO_3$ required to furnish 10 grams of silver from the following proportion:

$$\underset{(107.88)}{Ag} : \underset{(169.89)}{AgNO_3} = 10 : x$$

from which x, the weight of $AgNO_3$ required, is found to be 15.75 grams.

The advantage resulting from the use of test solutions of uniform, known strength lies in the fact that the sensitiveness of the test can be studied with better results. Some judgment can be formed of the relative amounts of each component present in a mixture if the preliminary work is carried out with solutions of known and uniform strength. In this way a qualitative analysis becomes an approximate quantitative one. The student should always exercise judgment in distinguishing traces from considerable quantities of a constituent found in the course of an analysis.

2. *Empirical Solutions.* The solutions resulting from dissolving solid samples and a great many of the reagent solutions represent another type, in that there is nothing uniform in regard to their strength, each individual solution being made up of a strength best suited for its particular use. These may be called empirical solutions. In this connection examine the list of re-

agents in the Appendix (pages 323–325). The concentration of these solutions may be expressed in grams of solute per liter or per milliliter. If expressed in grams of solute or its equivalent per milliliter, the term titre is sometimes applied. Thus a solution containing, for example, 0.050 gram of $PO_4^{\equiv}$ per milliliter is referred to as one having a phosphate titre of 0.050. The concept of titre is limited to the solutions and calculations of quantitative analysis.

3. *Per-Cent-by-Weight Solutions.* The strength of certain solutions is sometimes designated by the percentage by weight of solute contained in the solution. Thus a solution which contains, say, 20 grams of the solute in 100 grams of the solution is a 20 per cent solution.

4. *Designation by Means of Specific Gravity.* The specific gravity of a solution is sometimes used to indicate the strength of a reagent solution. This system is employed only in conjunction with the percentage by weight and necessitates the use of a specific gravity table for each kind of solution. The concentration of the common neutralization reagents, namely HCl, H_2SO_4, HNO_3 and NH_4OH is expressed in terms of the specific gravity with or without the corresponding percentage by weight.

To illustrate, the concentrated hydrochloric acid solution ordinarily supplied in the laboratory has a specific gravity of about 1.190. Reference to the specific gravity table in the Appendix (pages 334–335) shows that a solution of HCl of this specific gravity contains, at 15° C., 37.23 per cent of the solute, hydrogen chloride. One milliliter of this reagent, weighing 1.190 grams, will contain 0.3723×1.190 or 0.4430 gram of pure HCl.

To prepare a dilute solution of this acid for the usual laboratory uses, the amount of water to be added to the concentrated reagent must be calculated. A typical calculation of this kind is here given.

Suppose that it is desired to prepare a "dilute" hydrochloric acid reagent by dilution of 50 ml. of the concentrated reagent, so that the resulting solution will have a specific gravity of 1.100. How much water should be added?

Since the original solution has a specific gravity of 1.190 and contains 37.23 per cent of HCl by weight, the total weight of pure HCl in the 50 ml. will be

$$50 \times 1.190 \times 0.3723 = 22.15 \text{ grams of pure HCl}$$

The final solution should have a specific gravity of 1.100, which, from the table in the Appendix (pages 334–335) is found to contain 20.01 per cent of HCl. Letting x equal the weight and hence the volume of water to be added, we can express the calculation as follows:

$$22.15 = [(50 \times 1.190) + x]\,0.2001$$

that is, 20.01 per cent of the total weight of the mixture is pure HCl and we started with 22.15 grams of pure HCl. Solving, we find x equal to 51.2 grams of water; hence 51.2 ml. of water are to be used.

Special attention is called to the specific gravity table for ammonia solutions in the Appendix (page 333). Note that the percentage of solute is given in terms of NH_3 and not NH_4OH.

5. *Normal Solutions.* This system of concentration, extensively employed in quantitative analysis, is sometimes used in qualitative analysis to designate the strength of reagent solutions. A normal solution contains a gram-equivalent weight of the solute per liter of solution. A gram-equivalent weight is that amount of reactant which will bring into reaction, directly or indirectly, 1.008 grams of hydrogen. A normal solution of any acid therefore contains 1.008 grams of replaceable hydrogen; if the acid is monobasic, such as HCl, HNO_3 or $HC_2H_3O_2$, the molecular weight in grams will furnish the required gram-equivalent weight of hydrogen. A normal solution of H_2SO_4 contains one-half the molecular weight of H_2SO_4 in grams per liter of solution. Corresponding definitions hold for normal solutions of bases, of precipitating agents and of oxidizing and reducing agents.

6. *Molar Solutions.* A molar solution contains the molecular weight in grams of the solute in a liter of solution. Although molar solutions are not usually employed as actual laboratory reagents, the units of concentration used, the gram-mole, or the corresponding terms gram-ion and gram-atom, are tremendously important in the mathematical treatment of all equilibria relationships.

7. *Molal Solutions.* A molal solution contains one gram-molecular weight of the solute in 1000 grams of the solvent. In discussing the freezing points and boiling points of solutions concentrations are always specified in this way.

Gram-Atom, Gram-Mole and Gram-Ion Quantities. A gram-atom or a gram-atomic weight of an element is a weight in grams equal to the atomic weight of that element. Thus, a gram-atom of sodium consists of 22.997 grams of sodium, since this number is the atomic weight of sodium. Likewise 35.457 grams of chlorine is 1 gram-atom of chlorine and 1.008 grams of hydrogen is 1 gram-atom of hydrogen. One-half of the atomic weight of an element in grams constitutes one-half a gram-atom; one-tenth of the atomic weight in grams, a tenth of a gram-atom, etc.

A gram-mole or a gram-molecular weight (sometimes simply called a mole) is the molecular weight of a substance in grams. One gram-mole of AgCl, for example, consists of 143.337 grams of this compound, this number being the molecular weight of AgCl. A gram-mole of HCl weighs 36.465 grams, and a gram-mole of NaOH, 40.005 grams. One-half of the molecular weight is a half-mole, and one-tenth of the molecular weight constitutes 0.1 of a gram-mole. Thus 0.5 of 36.465 or 18.233 grams of HCl is 0.5 of a gram-mole of HCl, and 3.647 grams of HCl is 0.1 of a gram-mole of HCl.

A gram-ion is the atomic or molecular weight of the ion in grams. That is, if the ions in a solution consist of charged *atoms*, such as Ag^+, H^+, Cl^-, etc., the atomic weight in grams of the element in question constitutes 1 gram-ion; if the ions consist of *charged groups of atoms*, such as the ammonium ion, NH_4^+, the nitrate ion, NO_3^-, the sulfate ion, $SO_4^{=}$, or the acetate ion, $C_2H_3O_2^-$, the molecular weight of the charged radical, in grams, constitutes a gram-ion. If, for example, a solution of HCl contains 1.008 grams of H^+ ion and 35.457 grams of Cl^- ion, there are present 1 gram-ion of hydrogen ions and 1 gram-ion of chloride ions; or, again, if a certain solution is made by dissolving 1 gram-molecular weight of $AgNO_3$ in water and the resulting solution is completely ionized into Ag^+ ions and NO_3^- ions, the solution will contain 1 gram-ion of Ag^+ ion (107.88 grams) and 1 gram-ion of NO_3^- ion (62.008 grams).

It is obvious that the three terms gram-atom, gram-mole and gram-ion are fundamentally alike and define the same kind of unit of measurement, or mass, differing only in that they refer to different conditions of matter. The gram-atom refers to the atomic state of an element, the gram-mole to a compound or uncharged radical and the gram-ion to an ionized atom or radical. This fine

distinction is one of exact definition rather than of any real difference in meaning.

These units are used to express the quantity or mass of substance, and are used in all equilibrium calculations. It is important that the student thoroughly understand the meaning of these units and how they are obtained from the usual gram weights. The conversion from gram weights to gram-atom, gram-mole or gram-ion quantities is made by dividing the gram weight by the atomic or molecular weight:

$$\frac{\text{Weight in grams}}{\text{Atomic or molecular weight}} = \begin{cases} \text{Gram-atom, gram-mole or} \\ \quad \text{gram-ion quantity} \end{cases}$$

For example, the gram-mole quantity of $AgNO_3$ represented by 16.98 grams of $AgNO_3$ is:

$$\frac{16.98}{169.89} = 0.1 \text{ of a gram-mole}$$

The gram-atom quantity of silver represented by 16.98 grams of $AgNO_3$ may be calculated either (1) by finding the weight of silver contained in the given weight of $AgNO_3$ and dividing this in turn by the atomic weight of Ag, or (2) more simply from the gram-mole quantity of $AgNO_3$; for, since 1 molecule of $AgNO_3$ contains 1 atom of Ag, 0.1 of a gram-mole of $AgNO_3$ contains 0.1 of a gram-atom of Ag.

Furthermore, if this quantity of $AgNO_3$ were dissolved in a sufficiently large volume of water to result in complete ionization, there would be present 0.1 of a gram-ion of Ag^+ ion.

Conversely, to convert quantities expressed in terms of gram-mole, gram-atom or gram-ion units to gram weights, multiply the quantity by the molecular or atomic weight of the molecule, atom, or charged radical.

Molar and Gram-Ion Concentrations. A molar solution has already been defined as one containing the molecular weight of the solute in grams in *1 liter of the solution.* If one-half the molecular weight in grams of the solute is present in a liter of the solution, the concentration of the solution is said to be 0.5 molar. In the case of $AgNO_3$ previously referred to, if 0.1 of a gram-mole of $AgNO_3$ per liter is present in a liter of the solution, the solution is 0.1 *M* with respect to the solute; we say that its molarity is 0.1.

If this $AgNO_3$ solution is completely ionized, the gram-ion concentration of Ag^+ ion as well as of NO_3^- ion is 0.1 of a gram-ion, i.e., C_{Ag^+} is 0.1 and $C_{NO_3^-}$ is likewise 0.1, the symbol C being used to designate concentration.

It should be carefully noted that the terms molar concentration and gram-ion concentration refer specifically to the amount of solute and of ions, respectively, in a liter of solution. The gram-mole and gram-ion *quantities* are identical with the molar and gram-ion *concentrations* only when the volume of solution is 1 liter. For volumes other than a liter, the concentration remains the same but the absolute quantity will be different. Thus, if 200 ml. of a $AgNO_3$ solution containing 0.1 gram-mole of dissolved $AgNO_3$ per liter is taken, there is present only two-tenths of the amount of solute, namely 0.02 gram-mole, but the solution is still a 0.1 molar solution.

When a solute ionizes to furnish two ions of the same kind and one of another kind as, for instance, in the case of $Ca(NO_3)_2$, which ionizes according to the scheme:

$$Ca(NO_3)_2 \rightleftharpoons Ca^{++} + 2NO_3^-$$

the gram-ion concentration of NO_3^- ion is twice that of the Ca^{++} ion.

If the solution is known to be incompletely ionized the gram-ion concentrations of the ions, as well as the gram-molar concentration of that portion of the solute which is not ionized, are readily found by multiplying the molarity of the solution by the degree of ionization. In the above case, suppose that a 0.1 M solution of $Ca(NO_3)_2$ is 85 per cent ionized. The concentration of the Ca^{++} ion is then 0.1×0.85 or 0.085 gram-ion, the concentration of the NO_3^- ion is 0.2×0.85 or 0.170 gram-ion and the concentration of the non-ionized $Ca(NO_3)_2$ is 0.1×0.15 or 0.015 gram-mole.

The Calculations of Qualitative Analysis. In the study of the fundamental theory and of the reactions of qualitative analysis, computations must frequently be made involving the concentrations of ions and non-ionized solutes, the use of various equilibrium constants, the effect of reagents, etc. In fact, the only effective way to understand thoroughly and apply properly the theoretical principles is through the use of numerical calculations. Equilibrium calculations of one kind or another are the most important

types of computations encountered in the study of qualitative analysis. In these calculations, the data such as equilibrium constants and ionic concentrations are small numbers, and it is more convenient to express such quantities in the exponential form rather than as decimal fractions.

The Use of Exponents in Calculation. The magnitude of a quantity is expressed in the exponential form by writing the digits as coefficients multiplied by 10 raised to the proper power. Thus the number 1000, which is the product of $10 \times 10 \times 10$, or ten cubed, is written 1×10^3. The number 0.001, the product of $0.1 \times 0.1 \times 0.1$, becomes 1×10^{-3}, and 0.00001 becomes 1×10^{-5}, the significant figure, in each of the above cases 1 or unity, appearing as the coefficient, and the negative exponent being one more than the number of zeros used to locate the decimal point in the decimal fraction. When more than one significant figure appears in the number, it is conventional to place the decimal point after the first digit in the coefficient and to adjust the negative exponent accordingly. For example, 0.0000182 is written 1.82×10^{-5}.

In the operations of multiplying, dividing, squaring, cubing, extracting square and cube roots, etc., the numbers are expressed in the exponential form and the coefficients are treated in the ordinary arithmetical manner. The exponents are added algebraically for a multiplication, doubled for squaring and tripled for cubing. In a division the exponents are subtracted algebraically; in extracting a square root, the exponent is divided by 2, and for a cube root the exponent is divided by 3.

REVIEW EXERCISES — SET 2

1. Calculate the number of grams of $Cu(NO_3)_2 \cdot 6H_2O$ which must be dissolved to make a liter of test solution containing 10 milligrams of Cu^{++} ion in each milliliter. What is the molar concentration of the solution? What is the gram-ion concentration of Cu^{++}, assuming complete ionization of the salt?

2. Calculate the molarity of each of the following concentrated reagents: HCl, HNO_3, H_2SO_4. (See Appendix, page 334.)

3. It is desired to prepare molar solutions of HCl, H_2SO_4 and NH_4OH. How many milliliters of the concentrated reagent must be diluted to a liter, in order to obtain solutions of the required strength? (See Appendix, page 334.)

4. If you wish to prepare a hydrochloric acid solution having a specific gravity of 1.12, how much water should you add to 200 ml. of a solution which contains 30.55 per cent by weight of HCl?

5. A molar solution of NaOH is 76.6 per cent ionized at 25° C. Calculate the grams of non-ionized NaOH, Na^+ ion and OH^- ion present in 1 liter.

6. What is the molarity of a solution containing 72 grams of HCl in a volume of 600 ml.? What weight of H_2SO_4 in 600 ml. would make a solution of the same molarity as the above solution of HCl?

7. Calculate the grams of compound required to make liter quantities of solutions of the following molarity:

(*a*) 1 *M* $AgNO_3$	(*c*) 0.5 *M* Na_2HPO_4
(*b*) 0.1 *M* $HC_2H_3O_2$	(*d*) 0.7 *M* K_2CrO_4

8. How much HCl, H_2SO_4 and HNO_3, respectively, can be neutralized by 10 grams of NaOH?

9. Express in the exponential form: 2,600,000; 0.00000083; 96,494; 0.000000006453; 745,900,000,000.

10. Express in the decimal form: 6.03×10^{23}; 1.59×10^{-19}; 2.4×10^{0}; 6.845×10^{-1}; 9.39×10^{-5}; 4.55×10^{10}.

REACTIONS AND CHEMICAL EQUATIONS

Ionic Nature of Reactions. The study of the reactions encountered in the procedures of qualitative analysis constitutes one of the most important parts of the student's work. In order to bring about sharp separations and distinctive tests the reactions utilized, in order to be of the greatest service, must go practically to completion. In an aqueous solution practically all reactions are ionic in nature and, in most cases, reach equilibrium when the reaction has run almost to completion. The chemical changes which take place are the reactions between the ions involved and not between the molecules of the reacting substances. In other words, we are concerned almost entirely with ionic reactions, and the most general application which we can make of the theory of ionization is to realize that these chemical changes are ionic in nature. The reactions therefore are represented as ionic equations and are not in molecular form. An example will make this clear. Suppose we take a solution of $AgNO_3$ and add to it dilute HCl. A curdy white precipitate of AgCl will at once form. The same result can be obtained by adding a solution of NaCl, NH_4Cl, $BaCl_2$ or other soluble chloride to a solution of any soluble silver salt. If the reaction were expressed in molecular form, as:

$$HCl + AgNO_3 = AgCl + HNO_3 \qquad (1)$$

it would imply reaction between molecules. But we have ample evidence supporting the theory of ionization showing that dilute

solutions of $AgNO_3$, HCl, $NaCl$, etc., are highly dissociated into their respective ions. The complete form in which reactions of this kind can be represented may be shown by the following schematic arrangement:

$$\begin{array}{llll} HCl & \rightleftharpoons H^+ & + & Cl^- \\ & \quad + & & + \\ AgNO_3 & \rightleftharpoons NO_3^- & & Ag^+ \\ & \quad \downarrow\uparrow & & \downarrow\uparrow \\ & \quad HNO_3 & & \underline{AgCl} \end{array}$$

The products formed by this double decomposition result from an interchange of ions of the original solutions. In view of the fact that one of the products in equation (1), nitric acid, is highly ionized there will be little or no tendency towards its formation. The other product, silver chloride, is only slightly soluble in the mixed solutions (a fact indicated by underscoring its formula). Silver ions and chloride ions thus unite and are removed in the form of an insoluble precipitate; this causes the reaction to go practically to completion. These are the ions that are affected in this reaction and this fact is expressed as a simple ionic equation:

$$Ag^+ + Cl^- = \underline{AgCl}$$

The student should early acquire this ionic point of view and consider all reactions, with but few exceptions, as taking place between the ions concerned.

Classification of Ionic Reactions. In general, it can be stated that an ionic reaction takes place, and in most cases runs practically to completion, whenever ionic concentrations are decreased. The concentration of the reacting ions can be diminished in one of two general ways, namely (1) by ions uniting and (2) by ions transferring one or more electrons. These are the two important classes of reactions. In the first class are included several types, the reaction taking place because:

a. A precipitate is formed, since, in the formation of a solid, ions are removed from solution.

b. A weakly ionized acid or base or, in rare cases, a weakly ionized salt is the product of the reaction. This type includes, as well, the reactions of hydrolysis. Neutralization reactions also come under this heading, since the fundamental reaction here is the union of H^+ and OH^- to form water, and closely allied to this

All of these terms are in more or less general use but in this book we shall favor the term "apparent valence."

An increase in apparent valence corresponds to a loss of electrons and a decrease to a gain of electrons. This is true whether the original apparent valence is positive or negative, provided the increase is considered algebraically; that is, if the original apparent valence is negative an increase corresponds to a decrease in the numerical value. To illustrate, a change in apparent valence from -3 to -6 is an algebraic decrease and represents a reduction.

The Balancing of Redox Equations. Redox equations are often the cause of such great difficulty that many students try to evade the issue by attempting to memorize the equations encountered in the schemes of analysis. Aside from its possible value as a memory exercise this method of attack is to be condemned because it is so inefficient and unnecessary. A little mental effort devoted to understanding the ideas involved in writing these equations and to learning a systematic method of balancing them will enable one to handle any equation ordinarily encountered in analytical work and render any attempt to remember the complete equation not only useless but absurd.

The fundamental fact upon which all systematic methods of balancing are based is that oxidation and reduction always take place in equivalent amounts; that is, exactly the same number of electrons is lost by the reducing agent as is gained by the oxidizing agent. Any scheme for evaluating the number of electrons transferred therefore constitutes a method of balancing such equations. We shall consider only two of the many methods that have been proposed for accomplishing this: the ion-electron method and the valence-electron method.

The Ion-Electron Method. Let us take as an example the oxidation of a solution of $FeCl_2$ by a solution of potassium dichromate acidified with HCl. We know that the ferrous ion is here oxidized to the ferric ion whereas the dichromate ion is reduced to the chromic ion; since H^+ ions and the oxygens from the $Cr_2O_7^=$ ion are also involved, water will be formed in the reaction. The unbalanced equation in ionic form can now be set down:

$$Fe^{++} + Cr_2O_7^= + H^+ \rightarrow Fe^{+++} + Cr^{+++} + H_2O$$

The components in this equation are now resolved into their two separate equations, that for the oxidation of Fe^{++} being:

$$Fe^{++} \rightarrow Fe^{+++}$$

and for the reduction of the dichromate ion:

$$Cr_2O_7^{=} + H^+ \rightarrow Cr^{+++} + H_2O$$

The number of electrons associated with each equation must now be assigned. It is simple to see that the oxidation of a ferrous ion to the ferric ion is the result of the former having lost a single electron, whether we arrive at this decision by saying that 2 positive charges on the Fe^{++} ion now become 3 positive charges on the Fe^{+++} ion or whether we say that the valence has been changed from $+2$ to $+3$, since in this case the valence states are indicated by the number of charges carried by these ions. The half-cell or electron equation is therefore:

$$Fe^{++} = Fe^{+++} + 1e$$

The balancing of the half-cell equation for the reduction of the dichromate ion is not quite so simple. The way in which one determines the number of electrons which are transferred to the dichromate ion distinguishes the ion-electron method from other balancing methods. The rule here is first to balance *chemically*; that is, with respect to the number of atoms of each element involved. Since there are 2 chromium and 7 oxygen atoms in the Cr_2O_7 radical, the reaction calls for $14H^+$ giving $2Cr^{+++}$ and $7H_2O$:

$$Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O$$

The equation is next balanced *electrically*; that is, the number of electrons required is ascertained. The $(Cr_2O_7)^{=}$ ion, as a whole, has 2 negative charges; the $14H^+$ ions have a total of 14 positive charges, giving a net charge on the left side of the equation of $+12$. On the right side of the equation there are 2 chromic ions, each with 3 positive charges, or a total of $+6$. In order to have the equation, as a whole, electrically neutral, 6 negative charges, i.e., 6 electrons must be supplied. The balanced half-cell or electron equation is therefore:

$$(Cr_2O_7)^{=} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$

These 6 electrons are furnished by the ferrous ions and since each Fe^{++} ion loses 1 electron, there are required $6Fe^{++}$ to effect the reduction of the dichromate ion.

The two half-cell equations are finally added:

$$\begin{array}{r}
Cr_2O_7^{=} + 14H^+ + \cancel{6\epsilon} = 2Cr^{+++} + 7H_2O \\
6Fe^{++} = 6Fe^{+++} + \cancel{6\epsilon} \\
\hline
Cr_2O_7^{=} + 14H^+ + 6Fe^{++} = 2Cr^{+++} + 7H_2O + 6Fe^{+++}
\end{array}$$

cancelling the electrons which are transferred and giving the final, complete equation in ionic form.

If it becomes desirable or necessary to transform the ionic equation into a molecular one, the non-essential ions can easily be inserted by inspection and associated with their proper partners in the form of molecules. In the equation just written the ions not included are $2K^+$ from the $K_2Cr_2O_7$, $14Cl^-$ from 14HCl and $12Cl^-$ from $6FeCl_2$. These are paired off to give $2CrCl_3$, $6FeCl_3$ and 2KCl. The balanced equation in molecular form is therefore:

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 2CrCl_3 + 6FeCl_3 + 7H_2O + 2KCl$$

Rules for Using the Ion-Electron Method. 1. If the original unbalanced equation is presented in molecular form, the products being given, strip the equation of its non-essential or incidental ions and rewrite the equation in ionic form. If the reagents which are brought together and the essential products of the reaction are stated or known, set down only the essential ions and products as an unbalanced ionic equation. It is necessary, of course, to know in any case what the reduction and oxidation products are.

2. The oxidizing agent and the product to which it is reduced are then picked out and set down as a skeleton equation; likewise for the reducing agent and the product to which it is oxidized. For the example selected:

$$Cr_2O_7^{=} \rightarrow Cr^{+++} \quad \text{(reduction equation)}$$

$$Fe^{++} \rightarrow Fe^{+++} \quad \text{(oxidation equation)}$$

This step, which necessitates the recognition of the oxidizing and reducing agents, is the most troublesome part of this, as of any, method of handling redox equations. Suggestions will be given later for making it easier, but there is no way to remove entirely

the requirement of a background of specific chemical information in dealing with it.

3. Next, balance the equations chemically, so that there are the same number of atoms of each element on each side of the equation. No difficulty is encountered in those cases in which only one element in an ion is involved, but generally where oxy-ions are concerned, H^+, OH^- or H_2O must be introduced. If it is definitely known that the reaction proceeds in an acid solution, H^+ ions are supplied to the left side of the equation and H_2O is one of the products of the reaction; or, in an alkaline medium, OH^- ions appear as initial reactants. In the case illustrated the reduction equation becomes:

$$Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O$$

4. Evaluate the electron gain or loss in the reaction by finding the algebraic sum of the ion charges on the right and subtracting it algebraically from the sum found similarly for the ions on the left (this is the distinctive feature of this method). It is absolutely necessary to have the proper charge attached to each ion before evaluating the electron transfer. This evaluation can easily be carried out mentally.

5. Multiply each equation by factors which will give the same number of electrons lost by the reducing agent as are gained by the oxidizing agent, and then add the two half-cell equations; this step cancels the electrons.

6. If it is desired to include the incidental ions, i.e., to write the equation in molecular form, this may be done by adding to both sides of the balanced ionic equation a sufficient number of each incidental ion to put it in the form of the original unbalanced equation.

The Valence-Electron Method. This method differs from the ion-electron method in that the number of electrons involved is determined on the basis of apparent valence changes of the atoms concerned rather than on an electrical balance of charges on the ions as a whole. For the purpose of comparison, the same reaction, namely, the oxidation of $FeCl_2$ by an HCl solution of $K_2Cr_2O_7$ will be given. In ionic unbalanced form the reaction is written:

$$Fe^{++} + Cr_2O_7^{=} + H^+ \rightarrow Fe^{+++} + Cr^{+++} + H_2O$$

As before, the equation for the oxidation of Fe^{++} can readily be balanced:

$$Fe^{++} = Fe^{+++} + 1e$$

since the valence is increased from +2 to +3, requiring the loss of 1 electron.

The balancing of the half-cell equation for the reduction of the dichromate ion, by the valence-electron method, is based upon determining the number of electrons needed, as determined by the apparent change in valence undergone by the chromium atom. In $K_2Cr_2O_7$ or in the ion, $Cr_2O_7^{=}$, the "apparent valence" of each chromium atom is +6; we say that chromium here has an oxidation number of +6. This is deduced from the fact that each oxygen atom has a valence of −2 and each potassium atom a valence of +1, leaving +12 for both chromium atoms or +6 per atom of chromium. In the chromic ion, Cr^{+++}, the chromium has a valence of +3. We have, therefore, in the partly completed equation:

$$\underset{(2 \times 6 = 12+)}{Cr_2O_7^{=}} + H^+ \rightarrow \underset{(2 \times 3 = 6+)}{2Cr^{+++}} + H_2O$$

2 chromium atoms each suffering a valence decrease of +3 or a total of +6. This calls for 6 electrons. The 7 oxygen atoms require 14 hydrogen ions, forming $7H_2O$. The completed half-cell equation can now be written:

$$Cr_2O_7^{=} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$

To balance the electrons transferred from the reducing to the oxidizing agent requires multiplication of the $Fe^{++} - Fe^{+++}$ reaction by 6. Adding the two equations gives the final balanced ionic equation:

$$Cr_2O_7^{=} + 14H^+ + \cancel{6e} = 2Cr^{+++} + 7H_2O$$

$$6Fe^{++} = 6Fe^{+++} + \cancel{6e}$$

$$Cr_2O_7^{=} + 14H^+ + 6Fe^{++} = 2Cr^{+++} + 7H_2O + 6Fe^{+++}$$

Another Example. Another example of balancing redox equations will be helpful. If oxalic acid, $H_2C_2O_4$, a good reducing agent, is added to a solution of $KMnO_4$ acidified with dilute H_2SO_4, reduction of the permanganate takes place, with liberation of CO_2.

The reaction may be expressed, in molecular form, by the following unbalanced equation:

$$KMnO_4 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + H_2O + CO_2 + K_2SO_4$$

Rewriting this in ionic form to show only the ions and molecules actually concerned in the reaction, we have:

$$MnO_4^- + H^+ + C_2O_4^= \rightarrow Mn^{++} + H_2O + CO_2$$

The equations for the oxidizing agent and for the reducing agent are next set up. The MnO_4^- ion requires the presence of H^+ ions for its reduction to Mn^{++}. Accordingly, the components are assembled for this equation:

$$MnO_4^- + H^+ \rightarrow Mn^{++} + H_2O$$

By the ion-electron method, the chemical balance requires $8H^+$ for the 4 oxygen atoms in the MnO_4^-, giving $4H_2O$:

$$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$$

The electrical charges are now $+8$ on the hydrogen ions and -1 on the MnO_4^- ion, or a total of $+7$ on the left side of the equation; but 2 positive charges remain on the manganous ion, the water being, of course, electrically neutral. To equalize the charges on both sides of the equation 5 electrons are required:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O \qquad (1)$$

The balancing of this half-cell equation might also be done by the valence-electron method. In $KMnO_4$ or in the MnO_4^- ion, the manganese has an apparent valence or oxidation number of $+7$, but in Mn^{++} it is $+2$. There is a loss of 5 positive charges, requiring 5 electrons. As before, the chemical balance of atoms requires 8 hydrogen ions for the 4 oxygens, yielding $4H_2O$. The balanced half-cell equation is then as given above (equation 1).

The reducing ion, $C_2O_4^=$, is oxidized to CO_2. The equation for this change is easily balanced chemically:

$$C_2O_4^= \rightarrow 2CO_2$$

and using the ion-electron method, since 2 negative charges are associated with the $C_2O_4^=$ ion and the oxidation product, CO_2, is electrically neutral, 2 electrons are lost, giving the balanced half-cell equation:

$$C_2O_4^= = 2CO_2 + 2e \qquad (2)$$

One might also balance this equation by the valence-electron method, but not so simply. In the formula $H_2C_2O_4$, each carbon atom has an average apparent valence of $+3$, since there are $4O^{=}$ or $8-$ charges, offset by $2+$ charges on the hydrogen atoms, giving $+6$ for both carbons or $+3$ for each carbon atom. In CO_2 each carbon has a valence of $+4$. There is thus an increase of apparent valence of $+1$ for each carbon atom or a total of $+2$, corresponding to the loss of 2 electrons.

To balance the electrons transferred from the reducing ion to the oxidizing ion, equation (2) must be multiplied by 5 and equation (1) by 2; these, when added together and the electron cancelled, give:

$$5C_2O_4^{=} = 10CO_2 + \cancel{10e}$$

$$2MnO_4^{-} + 16H^{+} + \cancel{10e} = 2Mn^{++} + 8H_2O$$

$$\overline{2MnO_4^{-} + 16H^{+} + 5C_2O_4^{=} = 2Mn^{++} + 8H_2O + 10CO_2}$$

To restore this ionic equation to the original molecular equation, in order to show how much of the two acids, H_2SO_4 and $H_2C_2O_4$, is required, it is merely necessary to assign $10H^{+}$ to the $5C_2O_4^{=}$; the remaining $6H^{+}$ are furnished by $3H_2SO_4$. The $2MnO_4^{-}$ ions correspond to $2KMnO_4$. Two $SO_4^{=}$ ions account for $2MnSO_4$, and $2K^{+}$ with the third $SO_4^{=}$ are written as K_2SO_4. It is thus found that 2 moles of $KMnO_4$ react with 5 moles of $H_2C_2O_4$, involving at the same time 3 moles of H_2SO_4:

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + 8H_2O + 10CO_2 + K_2SO_4$$

Some Suggestions for Balancing Redox Equations. To aid in picking out oxidizing and reducing agents the following hints may be useful, provided the complete, unbalanced equation is available.

1. K^{+}, Na^{+}, Ca^{++}, Sr^{++}, Ba^{++}, Al^{+++} and other ions of this type are never involved in oxidiation-reduction reactions and should be ignored. Be on the lookout for such ions and compounds as MnO_4^{-}, $CrO_4^{=}$ or $Cr_2O_7^{=}$, NO_2^{-}, Cl^{-} or Cl_2, Br^{-} or Br_2, I^{-} or I_2, $S^{=}$ or H_2S, H_2O_2, $SO_3^{=}$, Fe^{++} or Fe^{+++}, and the like. Other examples are listed in Tables III and IV. If any of these substances are present they are almost certain to be involved in the reaction.

2. Look for an element which is present in the elementary form on one side of the equation. Such an element is certain to be involved. The half-cell equation is then formed by using the free element and the ion in which it is present on the other side of the equation.

3. Many oxy-ions are either oxidizing or reducing agents, and some may even be reduced or oxidized to other oxy-ions of the same element.

If the products of the reaction are not known, only experimental evidence can supply them with certainty. For common oxidizing and reducing agents, however, the behavior is so well known that the products can be predicted correctly in almost all cases. Some information on which such a prediction may be based is given in the discussion of oxidizing and reducing agents.

If there is doubt as to whether or not a particular substance is ionized, no error will be introduced by using it in either the ionized or the non-ionized form. The complete oxidation of H_2S, for example, may be formulated with equal accuracy as far as the application of the method is concerned as:

$$H_2S + 4H_2O \rightarrow 10H^+ + SO_4^=$$

or

$$S^= + 4H_2O \rightarrow 8H^+ + SO_4^=$$

If a reaction is known to take place in basic solution it is preferable to use OH^- ions and H_2O in balancing the half-cell equation as follows:

$$2OH^- \rightleftharpoons [O] + H_2O$$

If, however, it is not known that the reaction requires an alkaline environment and H^+ and H_2O are used in the balancing procedure, H^+ will appear among the products on the right in the balanced ionic equation. When this situation occurs, hydroxyl ions equal in number to the hydrogen ions are added to both sides of the equation. The H^+ and OH^- on the right are then combined into H_2O and the appearance of OH^- on the left then indicates the necessity of a basic solution, when this was not known in the beginning.

Sometimes two elements in the same compound are oxidized or reduced, as when As_2S_3 or Cu_2S is dissolved in HNO_3. Such cases are handled easily by keeping the constituents in the stoichi-

ometric relations indicated by the formula (2As to 3S; 2Cu to 1S) and proceeding with the balancing in the usual way.

Sometimes the same substance acts both as the oxidizing agent and as the reducing agent, i.e., oxidizes and reduces itself. An example is the transformation of a hypochlorite into a chlorate and a chloride:

$$KOCl \rightarrow KClO_3 + KCl$$

Such an equation is balanced by a direct application of the ion-electron method, the ion in question being used in both half-cell equations:

$$OCl^- + 2H_2O + 4e \rightarrow ClO_3^- + 4H^+$$

$$OCl^- + 2H^+ + 2e \rightarrow Cl^- + H_2O$$

Then,

$$3OCl^- + 2H_2O + 4H^+ \rightarrow ClO_3^- + 2Cl^- + 2H_2O + 4H^+$$

or

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

In the molecular form:

$$3KOCl \rightarrow KClO_3 + 2KCl$$

Sometimes a certain ion may be present in the unbalanced molecular equation both as an essential and as an incidental ion. This is frequently true of $SO_4^=$, Cl^- and NO_3^-. For example, if we compare the balanced ionic equation:

$$3SO_3^= + Cr_2O_7^= + 8H^+ \rightarrow 3SO_4^= + 2Cr^{+++} + 4H_2O$$

with the balanced molecular equation:

$$3Na_2SO_3 + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3Na_2SO_4 + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

it will be noticed that of the 7 $SO_4^=$ ions on the right in the latter equation only 3 are included in the ionic equation. These 3 are essential whereas the other 4 are purely incidental.

Oxidizing and Reducing Agents. In considering what ions and substances can be oxidized or reduced or, conversely, what ions or other substances constitute reducing and oxidizing agents, it must, in the first place, be remembered that many of the cations and most of the anions, present in the test solutions and in known mixtures and in samples, have either oxidizing or reducing tenden-

cies. For example, Sn^{++}, Fe^{++}, AsO_2^-, I^-, Br^-, $SO_3^{=}$, $S_2O_3^{=}$, $S^{=}$, $C_2O_4^{=}$ and CN^- are strong reducing ions; on the other hand, such ions as Fe^{+++}, $AsO_4^{\equiv}$, $Cr_2O_7^{=}$ and MnO_4^- are strongly oxidizing. Ions of this kind become oxidized or reduced by the addition to the solution of oxidizing or reducing agents. In the second place, the addition of an oxidizing or a reducing *reagent* may be either for the express purpose of causing a desired oxidation or reduction or, on the other hand, it may be for some other reason, the accompanying oxidation or reduction being merely an incidental effect.

TABLE III

COMMON OXIDIZING AGENTS

Substance Used	Element or Radical Involved	Apparent Valence of Element	Reduced to	Apparent Valence of Element in Product	Decrease in Apparent Valence	Gain in Electrons per Atom
Cl_2	Cl	0	Cl^-	−1	1	1
Br_2	Br	0	Br^-	−1	1	1
I_2	I	0	I^-	−1	1	1
NaOCl	OCl^-	+1	Cl^-	−1	2	2
Aqua regia	NO_3^-	+5	NO	+2	3	3
HNO_3 (dilute)	NO_3^-	+5	NO	+2	3	3
HNO_3 (conc.)	NO_3^-	+5	NO_2	+4	1	1
Na_2O_2	O (or $O_2^{=}$)	−1	$O^{=}$(or OH^-)	−2	1	1
H_2O_2	O (or $O_2^{=}$)	−1	$O^{=}$(or OH^-)	−2	1	1
$NaBiO_3$	BiO_3^-	+5	Bi^{+++}	+3	2	2
$KMnO_4$ (acid)	MnO_4^-	+7	Mn^{++}	+2	5	5
$KMnO_4$ (basic)	MnO_4^-	+7	MnO_2	+4	3	3
$K_2Cr_2O_7$ (acid)	$Cr_2O_7^{=}$	+6	Cr^{+++}	+3	3	3
K_2CrO_4 (basic)	$CrO_4^{=}$	+6	Cr^{+++}	+3	3	3

For example, stannous chloride is utilized as a reducing agent in the test for mercury; bromine is sometimes employed to oxidize iron to the ferric condition; $KMnO_4$ to oxidize the oxalate ion, etc. But H_2S, for example, used as a precipitating agent, will also act as a reducing agent toward any oxidizing ions present in the solution. HNO_3, if used as a solvent, will also function as an oxidizing agent; in fact, its effective solvent action is attributable to its strong oxidizing tendency.

The more important and frequently used reagents which have

oxidizing ability are listed in Table III. The table gives the form in which the reagent is supplied, the element or ion responsible for the oxidation, its reduction product, and the apparent valence of the element in its oxidized and reduced form, together with the number of electrons gained per ion. Reducing reagents are tabulated in Table IV in the same way.

Some comment on these reagents should be helpful in balancing redox equations involving these substances. The important matter to bear in mind is the writing and balancing of the half-cell reactions concerned.

TABLE IV

COMMON REDUCING AGENTS

Substance Used	Element or Radical Involved	Apparent Valence of Element	Oxidized to	Apparent Valence of Element in Product	Increase in Apparent Valence	Loss of Electrons per Atom
$FeSO_4$	Fe^{++}	+2	Fe^{+++}	+3	1	1
$SnCl_2$	Sn^{++}	+2	Sn^{++++} (as $SnCl_6^{=}$)	+4	2	2
H_2S	$S^{=}$	−2	S	0	2	2
H_2S	$S^{=}$	−2	$SO_4^{=}$	+6	8	8
Na_2SO_3	$SO_3^{=}$	+4	$SO_4^{=}$	+6	2	2
$NaAsO_2$	AsO_2^{-}	+3	$AsO_4^{\equiv}$	+5	2	2
$H_2C_2O_4$	$C_2O_4^{=}$	+3	CO_2	+4	1	1
KI	I^{-}	−1	I_2	0	1	1
H_2O_2	O (or $O_2^{=}$)	−1	O_2	0	1	1
Metals, e.g., Zn	Zn	0	Zn^{++}	+2	2	2
Hydrogen	H_2	0	H^{+}	+1	1	1

The Halogens. In the form of the free element Cl_2, Br_2 and I_2 are oxidizing agents, and are reduced to the simple anion form. For example, the change for iodine is:

$$I_2 + 2e = 2I^-$$

The iodide ion, I^-, and the bromide ion, Br^-, are reducing agents. The former is frequently supplied in analytical procedures in the form of NH_4I or KI:

$$2I^- = I_2 + 2e$$

Free chlorine, NaOCl and $KClO_3$, are all oxidizing substances which are reduced to Cl^-. The half-cell equations are:

$$Cl_2 + 2e = 2Cl^-$$

$$ClO^- + 2H^+ + 1e = Cl^- + H_2O$$

$$ClO_3^- + 6H^+ + 4e = Cl^- + 3H_2O$$

Nitric Acid. This oxidizing solvent is frequently used in dissolving certain sulfides and metals. When the acid is dilute, the NO_3^- ion is reduced to NO:

$$NO_3^- + 4H^+ + 3e = \overline{NO} + 2H_2O$$

If the acid is concentrated, the reduction product is NO_2:

$$NO_3^- + 2H^+ + 1e = \overline{NO_2} + H_2O$$

Aqua Regia. This is a mixture of concentrated HNO_3 and concentrated HCl. The solution contains NO_3^-, Cl^- and H^+ ions, and owes its oxidizing ability to NO_3^- which is reduced, as in nitric acid, to NO. When this reagent decomposes, according to the reaction

$$NO_3^- + 2Cl^- + 4H^+ = NOCl + Cl_2 + 2H_2O$$

the free chlorine which is liberated may exert a strong oxidizing effect.

Potassium Permanganate. This very strong oxidizer may be reduced, by a reducing agent, either to hydrated MnO_2 or else to Mn^{++}. The former reaction takes place in an alkaline or neutral solution, according to the half-cell equation:

$$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$$

In an acid medium, the reaction (already given on page 40) is:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

This is a case where the product of the reduction is determined by the acidity or alkalinity of the medium.

Chromates and Dichromates. A somewhat similar situation exists in the case of the chromates and dichromates, the difference being that here it is the formula of the reactant and not that of the product which is determined by the acid or basic nature of the

medium. The form of the ion present is solely dependent upon the acidity of the solution, as can be seen from the equations:

$$Cr_2O_7^{=} + 2OH^- \rightleftharpoons 2CrO_4^{=} + H_2O$$

and

$$2CrO_4^{=} + 2H \rightleftharpoons Cr_2O_7^{=} + H_2O$$

Hence, in alkaline solution the chromate ion predominates; in acid solution the dichromate ion predominates.

REVIEW EXERCISES — SET 3

1. Classify ionic reactions on the basis of the product formed.

2. Define and illustrate: valence; oxidation; reduction; "half-cell" reaction.

3. Write equations showing how the following electrolytes ionize: (*a*) H_2SO_4; (*b*) $K_2Cd(CN)_4$; (*c*) $NaHZnO_2$; (*d*) As_2S_5.

4. Rewrite the following molecular equations, giving the essential ions involved, and then balance the equations:

(*a*) $Hg_2(NO_3)_2 + NaCl = \underline{Hg_2Cl_2} + NaNO_3$

(*b*) $Na_2SO_3 + HCl = \overline{SO_2} + H_2O + NaCl$

(*c*) $PbSO_4 + NH_4C_2H_3O_2 = \underset{\text{(non-ionized)}}{Pb(C_2H_3O_2)_2} + (NH_4)_2SO_4$

(*d*) $Al_2S_3 + HOH = \underline{Al(OH)_3} + \overline{H_2S}$

5. What is the apparent valence of the indicated element in each of the following compounds:

(*a*) Mn in $MnSO_4$, H_2MnO_3, Na_2MnO_4, $KMnO_4$
(*b*) Cr in $CrCl_2$, $NaCrO_2$, K_2CrO_4, CrO_3
(*c*) S in H_2S, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4
(*d*) N in HNO_2, HNO_3, NH_3, N_2O

6. Balance the equations in the following exercises:

(*a*) $Cr_2O_7^{=} + I^- + H^+ = Cr^{+++} + I_2 + H_2O$
(*b*) $MnO_4^- + I^- + H^+ = Mn^{++} + I_2 + H_2O$
(*c*) $AsO_4^{\equiv} + I^- + H^+ = AsO_3^{\equiv} + I_2 + H_2O$
(*d*) $NO_3^- + S^{=} + H^+ = NO + S^0 + H_2O$

7. (*a*) $Bi^{+++} + SnO_2^{=} + OH^- = Bi^0 + SnO_3^{=} + H_2O$
(*b*) $MnO_4^- + S^{=} + H^+ = Mn^{++} + S^0 + H_2O$
(*c*) $PbO_2 + Mn^{++} + H^+ = Pb^{++} + MnO_4^- + H_2O$
(*d*) $Cr_2O_7^{=} + NO_2^- + H^+ = Cr^{+++} + NO_3^- + H_2O$

8. (*a*) $HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$
(*b*) $KMnO_4 + H_2SO_3 = MnSO_4 + H_2SO_4 + K_2SO_4 + H_2O$
(*c*) $HNO_3 + Bi_2S_3 = Bi(NO_3)_3 + S^0 + NO + H_2O$
(*d*) $KI + Cl_2 = I_2 + KCl$

9. (a) $I_2 + H_2S = S + HI$
(b) $K_2Cr_2O_7 + H_2S + HCl = CrCl_3 + KCl + S^0 + H_2O$
(c) $KMnO_4 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + K_2SO_4 + CO_2 + H_2O$
(d) $Na_2O_2 + Fe(OH)_2 + H_2O = Fe(OH)_3 + NaOH$

10. (a) $PbS + HNO_3 = PbSO_4 + NO + H_2O$
(b) $HgS + HNO_3 + HCl = HgCl_2 + S^0 + NO + H_2O$
(c) $Na_2O_2 + Mn(OH)_2 + H_2O = MnO(OH)_2 + NaOH$
(d) $Sb_2S_5 + HCl = SbCl_3 + S^0 + H_2S$

THE LAW OF CHEMICAL EQUILIBRIUM

Reaction Velocity. The speed with which chemical changes take place varies widely for different reacting substances. Thus the rusting of iron at ordinary temperatures is a comparatively slow reaction, but many other reactions take place practically instantaneously. By reaction velocity is meant the amount of reactant transformed in unit time. Reaction velocities can be measured experimentally by determining the amount of substance which is used up or formed during definite intervals of time under definite, specified conditions. For the same reacting substances the velocity of reaction depends upon such factors as temperature, pressure and amount of substance present. Increase of temperature speeds up all reactions, the velocity being about doubled for every 10° C. rise in temperature. The influence of changes in temperature and pressure on a reacting system which has come to equilibrium will be taken up later.

The amount of substance present and capable of reacting is a very important factor influencing the rate of reaction. The effect of the concentration of the reacting components on the speed of the reaction, called **mass action**, is of fundamental importance in the study of chemical changes.

Mass Action. The substances undergoing change in a reaction are known as the **active masses** or the concentrations, the actual quantity being expressed in gram-moles or gram-ions. The amount of substance transformed in unit time depends upon the amount of each reactant present, temperature and other factors remaining constant. Doubling the amount of one reactant will necessarily result in more being transformed into the products of the reaction. The effect of the mass on the reaction velocity is called **mass action** and the generalization, which follows from this, can be stated thus: **The velocity of a reaction is proportional to the**

active masses present at any instant. Suppose a given number of molecules of the substance A are reacting with a like number of molecules of B. The rule states that the rate at which A will react with B is proportional to the amounts of A and B present. The reaction velocity will therefore be equal to the product of the molar concentrations of A and B times a proportionality factor, k (velocity constant), characteristic of this particular reaction. Algebraically this can be represented thus:

Reaction velocity = molar concentration of A $\times$ molar concentration of B $\times$ k

or, more simply, if we let C stand for the molar concentration of any particular reacting component and v for the reaction velocity:

$$v = C_A \times C_B \times k$$

If two molecules at A react with one of B the expression becomes:

$$v = C_A \times C_A \times C_B \times k$$

or, squaring the concentration of A:

$$v = (C_A)^2 \times C_B \times k$$

In general, if n parts of A react with m parts of B the general velocity equation is expressed thus:

$$v = (C_A)^n \times (C_B)^m \times k$$

the total molar concentration of each component being raised to a power equal to the coefficient representing the number of like reacting molecules or ions.

Reversibility of Reactions. The extent to which a reaction will proceed in one direction depends, among other factors, upon the nature of the products formed. If the newly formed products show any tendency of interacting among themselves to reform the initial reactants an opposing action will be set up in the reverse direction and the net effect will be that the entire amounts of the initial components are not transformed when the reaction appears to stop. Some reactions show a marked tendency to reverse, so much so that they are of little value in analytical chemistry. In other reactions, reversibility is less pronounced and here the reactions run nearly, but *not entirely*, to completion. These are the analytically useful ones, as will be emphasized later.

All reactions are reversible to a certain extent. This point cannot be overemphasized because it is the basis upon which the fundamental theory rests.

Equilibrium. In all reacting systems, therefore, a condition will be reached where a certain, even though small, concentration of the initial reactants can exist side by side with the products of the reaction apparently without having further change take place. There is a state of equilibrium set up. It is a dynamic equilibrium and means that for any reversible reaction such as:

$$A + B \rightleftharpoons C + D$$

after equilibrium has been reached, the reactants A and B are reacting to form C and D at exactly the same rate that C and D are reacting to form A and B. Equilibria are set up in all sorts of reacting systems; for example, between gases, between dissolved molecules and their ions, between precipitates and the solution that surrounds them, and between substances distributed between two solvents. The fundamental law which gives expression to the state of equilibrium is called the Law of Chemical Equilibrium and is of extreme importance in the study of reactions. The theory of reactions is based on this law and it is the most fundamental principle with which we shall have to deal.

The Law of Chemical Equilibrium. In considering the reaction between A and B, we derived the algebraic expression for the reaction velocity, namely,

$$v_1 = C_A \times C_B \times k_1 \tag{1}$$

where C stands for the molar concentrations and k_1 is a velocity constant characteristic of the reaction between A and B. Suppose we apply a similar equation to another set of reacting substances, say to C and D. This will be characterized by a different velocity, v_2, and a different velocity constant, k_2:

$$v_2 = C_C \times C_D \times k_2 \tag{2}$$

Now suppose that the substances C and D are the products resulting from A and B and, vice versa, A and B are the products resulting from C and D as in the reversible reaction:

$$A + B \rightleftharpoons C + D$$

Hence C and D are forming during the reaction at a rate depend-

ent upon the amounts of A and B present. As A and B are used up their masses decrease and the reaction velocity in the direction of C and D decreases. But the amounts of C and D are continually increasing and will interact to reform A and B. When the amounts of C and D are in such proportions as to cause the reaction to reverse at the same rate that it is proceeding forward, a dynamic state of equilibrium is set up, as previously indicated. The velocities are then equal in both directions. We can then apply the velocity equations to a reaction going in both directions, at the point where the concentrations are in such proportions as to make the velocity forward equal to the velocity backward. If the two algebraic equations which express the relation between velocity and concentration are equated, we have:

$$v_F = C_A \times C_B \times k_1 = v_2 = C_C \times C_D \times k_2$$

Therefore,

$$C_A \times C_B \times k_1 = C_C \times C_D \times k_2$$

and dividing by $C_A \times C_B$ and transferring k_2, the equilibrium ratio is obtained:

$$\frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2}$$

The ratio of the products of the molar concentrations is then equal to the ratio of the velocity constants, when equilibrium is reached. The ratio k_1/k_2 can be designated K, and then becomes an equilibrium constant characteristic of this reaction. The equilibrium expression then is written:

$$\frac{C_C \times C_D}{C_A \times C_B} = K \quad \text{(equilibrium constant)}$$

If for every molecule or ion of B, 2 molecules or ions of A are required, the value of C_A is squared in the above expression; if three times, the value is cubed, and for the general reaction:

$$nA + mB \rightleftharpoons qC + rD$$

the most general expression for the equilibrium can be written:

$$\frac{(C_C)^q \times (C_D)^r}{(C_A)^n \times (C_B)^m} = K$$

The above expression states: **In a reacting system, when equilibrium is reached, the product of the molar concentrations of the products of the reaction divided by the product of the molar concentrations of the reactants (each concentration raised to a power equal to the coefficient representing the number of like reacting parts which enter into the reaction) is always equal to a constant. This is the Law of Chemical Equilibrium.** The expression given is in the most general form. It will take on modified forms in the several applications which follow. For each reaction for which the law strictly holds, at constant temperature and pressure, the numerical value of the equilibrium constant is always the same. No matter how much the concentration of any one component in the reaction mixture varies, the proportions of the other components must change until equilibrium is again established and the value of K restored. Thus if the amount of A is increased in the above reversible reaction, the reaction will run faster in the direction of the formation of C and D, more of these products will be formed, reaction will reverse at a faster rate than originally and again equilibrium will be established, with the proportions A, B, C and D changed but the ratio of the products of their molar concentrations still the same.

If the pressure on a system in equilibrium is increased, there will be a change in the proportions of the reacting components when the new equilibrium is established at the higher pressure. Of the two opposing reactions, that one will be favored which leads to a reduction in the volume of the system. This is particularly significant in gaseous reactions. There is thus a shift or displacement in the equilibrium concentrations, the system again coming to equilibrium with different proportions of the reacting components. A change of pressure, however, does not change the value of the equilibrium constant.

When the temperature of a reacting system in equilibrium is changed, there is a change in the value of the equilibrium constant; that is, a new ratio is established for the equilibrium concentrations at the new temperature. With a rise in temperature, the equilibrium is shifted in the direction favoring the reaction which absorbs heat. The system as a whole tends to oppose the effect of the added stress placed on it; it does this by favoring that reaction which uses up the heat supplied in raising the temperature.

The effect of changes in concentration, pressure and temperature on a system in equilibrium is summed up in a very general law known as Le Chatelier's Law, which states: **Whenever a stress is applied to a system in equilibrium, that reaction will be favored which tends to offset or annul the effect of the stress.** Thus, increasing the concentration of one reactant causes the reaction to proceed faster in order to lower this concentration. Increased pressure will be opposed by that reaction which tends to relieve the pressure by reducing the volume. Raising the temperature favors the reaction, which, by absorbing heat, tends to lower the temperature.

The Law of Chemical Equilibrium is of wide application to a great variety of reactions. It was first shown to hold for reactions between molecules of organic substances. It is also applied to molecular gas reactions. In the reactions of qualitative analysis a number of important ionic equilibria are encountered. These equilibria are discussed in the following sections. They will be taken up in the following order:

1. Ionization equilibria (ionization constants).
2. Equilibria of ions of precipitates (solubility product constants).
3. Equilibria of complex ions (instability constants).
4. Hydrolysis equilibria (hydrolysis constants).
5. Amphoteric equilibria.
6. Oxidation-reduction (redox) equilibria.

THE EQUILIBRIUM LAW APPLIED TO IONIZATION: IONIZATION CONSTANTS

The theory of ionization states that when electrolytes dissolve in water they are dissociated to a greater or less extent into positively charged cations and negatively charged anions. Ionization can be regarded as a reversible chemical reaction between dissolved molecules and their respective ions and when equilibrium is reached certain of the dissolved molecules are dissociating into ions at a reaction rate which is equal to the rate at which other ions combine to reform non-ionized molecules. We can indicate such an ionization reaction by means of the general equation:

$$MA \rightleftharpoons M^+ + A^-$$

where MA stands for the dissolved non-ionized molecules of the compound MA, M^+ for the cations and A^- for the anions in equilibrium with the non-ionized portion of the dissolved electrolyte. At equilibrium, which is quickly reached when the compound is dissolved, there will always be maintained a certain fixed ratio between the non-ionized molecules and the products of their ionization. The ratio of the concentrations of the initial and final products of a reaction is dealt with by the Law of Chemical Equilibrium and hence, in establishing the conditions for equilibrium for the ionization of weak electrolytes, the law finds here a very important application.

The general equilibrium formula:

$$\frac{C_C \times C_D}{C_A \times C_B} = K$$

which expresses the equilibrium ratio of concentrations in the general reaction:

$$A + B \rightleftharpoons C + D$$

may be transformed for the special reaction of ionization of the electrolyte MA:

$$MA \rightleftharpoons M^+ + A^-$$

into the special form:

$$\frac{C_{M^+} \times C_{A^-}}{C_{MA}} = K$$

The symbol K is an equilibrium ratio and expresses the ratio of the product of the ion concentrations to the concentration of the non-ionized portion of the solute.

Equilibrium Ratios and Ionization Constants. One can write such an equilibrium expression and calculate the numerical value of the ratio for any electrolyte, but the ratio will have the same constant value, for all ranges of concentration *for weakly ionized electrolytes only.* For highly ionized acids and bases and for salts, which, with few exceptions, are highly ionized, the ratio is not constant. For weakly ionized acids, such as $HC_2H_3O_2$, HCN and HNO_2, and for the weakly ionized NH_4OH, the ratio is constant for all concentrations. When the ratio is found to be constant for a weak electrolyte, this ratio is known as an **ionization constant.**

Thus for a weakly ionized monobasic acid HA which ionizes according to the equation:

$$HA \rightleftharpoons H^+ + A^-$$

the equilibrium is expressed by the relation:

$$\frac{\text{Concentration of H}^+ \text{ ions} \times \text{concentration of } A^- \text{ anions}}{\text{Concentration of non-ionized molecules}} = K \quad \text{(ionization constant)}$$

or in simpler form:

$$\frac{C_{H^+} \times C_{A^-}}{C_{HA}} = K_{(ion)}$$

As has already been stated, an electrolyte is characterized by a true ionization constant only if the equilibrium ratios calculated for a number of concentrations have the same numerical value, i.e., if the ratios are practically the same for all concentrations. **The Law of Chemical Equilibrium can be rigorously applied to ionic equilibria only for weak electrolytes.** Whether or not an electrolyte conforms to the law must be discovered by experiment and calculation.

The ionization constant, for any particular electrolyte of specified concentration, will vary with the temperature, since the extent of ionization varies with the temperature. Changes of pressure have little effect on the ionization constant. The method of calculating ionization constants, the effect of changes in concentration and of added substances and the way ionization equilibria are used in qualitative analysis are illustrated in the following paragraphs for the case of acetic acid, a typically weak electrolyte.

Ionization Equilibrium of $HC_2H_3O_2$

Calculation of the Constant. Suppose that we take a dilute aqueous solution of acetic acid of such strength that a liter contains one-tenth of a gram-mole (one-tenth of the molecular weight in grams or 6.0032 grams) of dissolved $HC_2H_3O_2$. As a weak electrolyte, it will be ionized to a small extent into H^+ ions and $C_2H_3O_2^-$ ions according to the equation:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

The actual degree of ionization at 18° C. is 1.34 per cent (given in Table I, page 15). The respective concentrations in a liter of

0.1 molar acetic acid are therefore 0.1 × 0.0134 or 0.00134 gram-ion of H^+; 0.1 × 0.0134 or 0.00134 gram-ion of $C_2H_3O_2^-$, and 0.1 × 0.9866 or 0.09866 gram-mole of non-ionized $HC_2H_3O_2$.

The equilibrium expression for this ionization is written:

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{(ion)}$$

Placing the numerical values for the concentrations of the reacting components in this expression gives the numerical ratio:

$$\frac{(0.1 \times 0.0134) \times (0.1 \times 0.0134)}{(0.1 \times 0.9866)} = 0.0000182$$

The value 0.0000182 or 1.82×10^{-5}, sometimes also written 0.0_4182, is the ionization constant for $HC_2H_3O_2$. If the equilibrium law holds rigorously for this electrolyte, this same numerical value must be obtained for acetic acid solutions of other concentrations. That this is the case is shown in the calculation below.

Effect of Dilution. Suppose we dilute the above 0.1 M solution to ten times its volume, thus making a 0.01 M solution of $HC_2H_3O_2$. One liter of this diluted solution will then contain only one-tenth as much dissolved solute as the first solution considered. If no change in the degree of ionization took place in this more dilute solution, a calculation of the ionization constant would give a new, different value for $K_{(ion)}$. We know, however, from our study of ionization that the extent of ionization increases with dilution, and this means that the equilibrium which became disturbed through dilution is again restored by adjustment of the ratio between the concentrations of the ions and non-ionized molecules. The value for the percentage of ionization of a 0.01 molar solution of $HC_2H_3O_2$ at 18° C. is 4.17 per cent (see Table II, page 16). The new concentrations are therefore 0.01 × 0.0417 or 0.000417 gram-ion of H^+, 0.01 × 0.0417 or 0.000417 gram-ion of $C_2H_3O_2^-$ and 0.01 × 0.9583 or 0.009583 gram-mole of non-ionized $HC_2H_3O_2$. Inserting these values in the equilibrium expression gives:

$$\frac{(0.01 \times 0.0417) \times (0.01 \times 0.0417)}{(0.01 \times 0.9583)} = 0.0000181$$

This value for the ionization constant is in very close agreement with the value calculated above for the 0.1 M solution and shows

that the equilibrium law can be rigorously applied to acetic acid solutions.

The method of calculating ionization constants must be mastered by the student, for frequent use is made of ionic equilibria throughout the experimental work. To calculate the constant for any electrolyte we must know the two quantities; namely, the molarity of the solution and the degree of ionization at the specified temperature, and it is well for the beginner to resolve each term into its two factors, as shown in the foregoing calculations.

The formula can be simplified by letting α stand for the fraction which is present as ions, $1 - \alpha$ for the non-ionized fraction and M for the total molar concentration of the dissolved solute. The expression then becomes:

$$\frac{M\alpha \times M\alpha}{M(1 - \alpha)} = K_{(\text{ion})}$$

$$M\left(\frac{\alpha^2}{1 - \alpha}\right) = K_{(\text{ion})}$$

In this form the relationship between dilution and degree of ionization is known as the **Ostwald Dilution Formula.**

If we know the ionization constant and the molar concentration of a dissolved solute we can calculate the degree of ionization by solving for α in the above equation. Since α must be very small for any substance to which this expression may be applied, $1 - \alpha$ will differ only slightly from 1 and so very little error will be introduced by dropping α from the denominator. We have then, approximately,

$$M\alpha^2 = K_{(\text{ion})}$$

or

$$\alpha = \sqrt{\frac{K_{(\text{ion})}}{M}}$$

Ionization Equilibria of Other Electrolytes

Acids. Other acids that follow the equilibrium law more or less closely, that is, those that are rather weakly ionized, are HCN, HNO_2, H_2S, H_2CO_3, $H_2C_2O_4$, H_3AsO_3, H_3AsO_4, H_3PO_4, H_3BO_3. The more strongly ionized acids, such as HCl, HNO_3 and H_2SO_4, do not yield the same constant for different concentrations and thus deviate from the law. With weakly ionized

dibasic acids, such as H_2S, H_2CO_3 and $H_2C_2O_4$, which ionize in two stages, there is a primary and a secondary ionization constant. With tribasic acids there is a primary, a secondary and a tertiary ionization constant, corresponding to the three stages of ionization (see Table I, page 15 and Table V, page 59). Thus, for H_3PO_4 we have:

$$\frac{C_{H^+} \times C_{H_2PO_4^-}}{C_{H_3PO_4}} = K_1 \quad \text{(primary ionization constant)}$$

$$\frac{C_{H^+} \times C_{HPO_4^=}}{C_{H_2PO_4^-}} = K_2 \quad \text{(secondary ionization constant)}$$

and

$$\frac{C_{H^+} \times C_{PO_4^{\equiv}}}{C_{HPO_4^=}} = K_3 \quad \text{(tertiary ionization constant)}$$

The equilibrium relationships of H_2S, a weakly ionized dibasic acid, are extremely important. This reagent is used in precipitating many metallic ions as sulfides and the amount of sulfide ion which this acid yields by its secondary ionization must be very carefully regulated. The case of H_2S will be fully discussed when we come to the precipitation of the cations of Groups II and III.

It has already been pointed out (page 15) that the primary ionization stage takes place to a much greater extent than the secondary, and the secondary more than the tertiary; and accordingly the H^+ ion concentration of acids is due largely to the primary ionization. Primary ionization constants of dibasic and tribasic acids are therefore numerically much larger figures than the secondary and tertiary constants. This will become evident from Table V. The smaller the degree of ionization, the smaller the constant and the more closely will the electrolyte obey the Law of Chemical Equilibrium.

Bases. The only commonly used base which can be considered as closely following the law is NH_4OH. The calculation of its ionization constant is not so simple a matter as that for acetic acid, because in a solution of ammonium hydroxide there are, besides a low concentration of NH_4^+ ions and OH^- ions, non-ionized dissolved NH_4OH and dissolved NH_3. For purposes of calculation we may write:

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = K_{(ion)}$$

Salts. Since salts, as a general rule, are strong electrolytes, no constants can be calculated. We can, of course, calculate a new value for each particular dilution, but on the basis of the theory here outlined, we cannot apply it in the same sense that we apply it, for example, to acetic acid and ammonium hydroxide.

TABLE V

IONIZATION CONSTANTS

Electrolyte	Primary	Secondary	Tertiary
HCl	*		
HNO_3	*		
HNO_2	5×10^{-4}		
$HCHO_2$	2×10^{-4}		
$HC_2H_3O_2$	1.8×10^{-5}		
HCN	7×10^{-10}		
H_2SO_4	*	3×10^{-2}	
$H_2C_2O_4$	3.8×10^{-2}	5×10^{-5}	
$H_2C_4H_4O_6$	9.7×10^{-4}	9×10^{-5}	
H_2SO_3	1.7×10^{-2}	1×10^{-7}	
H_2CO_3	3×10^{-7}	6×10^{-11}	
H_2S†	9×10^{-8}	1.2×10^{-15}	
H_3AsO_4	5×10^{-3}	4×10^{-5}	6×10^{-10}
H_3PO_4	1×10^{-2}	2×10^{-7}	4×10^{-13}
$HAsO_2$	6×10^{-10}		
H_3PO_3	6×10^{-10}		
H_3BO_3	7×10^{-10}		
HOH‡	2×10^{-16}		
$NaOH$	*		
NH_4OH	1.75×10^{-5}		
$Ca(OH)_2$	3×10^{-2}		

* Ionization too great to yield an ionization constant.

† $\frac{(C_{H^+})^2 \times C_{S^-}}{C_{H_2S}} = 1.1 \times 10^{-22}$; $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$.

‡ $C_H \times C_{OH^-} = 1.2 \times 10^{-14}$

COMMON-ION EFFECT

In the ionization equilibrium formula it should be noted that the numerator of the ratio is the *product* of the gram-ion concentrations of the ions involved. In the particular cases calculated above for $HC_2H_3O_2$ the concentration of the cation, H^+, is equal to the

concentration of the anion, $C_2H_3O_2^-$, merely because these values were obtained by measuring the ionization of pure solutions of $HC_2H_3O_2$. The fact that the concentrations of each set of ions need not necessarily be equal for equilibrium to be established has a very important application to actual analysis. The concentration of one set of ions may greatly exceed that of the other set of ions, and cases actually arise where it becomes desirable or necessary to add another compound containing ions of the same kind as the one or the other set already present. By this means the concentration of one ion can be adjusted to any desired value by varying the concentration of the other ion. The effect on the equilibrium of these added common ions is known as the **common-ion effect.** It is illustrated here in the case of $HC_2H_3O_2$.

Suppose we are carrying out an analytical procedure in an acidic solution and find it desirable to have a low concentration of hydrogen ions present. A weak acid such as $HC_2H_3O_2$ yields, we know, a low concentration of H^+, but a still lower concentration can be secured by adding a highly ionized salt of acetic acid such as $NH_4C_2H_3O_2$ or $NaC_2H_3O_2$ to the solution of acetic acid. The effect of the large addition of acetate ions to those already present is to greatly decrease the concentration of the hydrogen ions. That this must be the result can be seen from an actual calculation.

Suppose to a liter of 0.1 M $HC_2H_3O_2$ which ionizes to the extent of 1.34 per cent we add 0.1 of a gram-mole of $NaC_2H_3O_2$, which in a liter of solution at 18° C. ionizes about 80 per cent. We have at the start 0.00134 gram-ion of $C_2H_3O_2^-$ from the acetic acid and 0.080 gram-ion of the same ion from the added sodium acetate, or a total of 0.08134 gram-ion of $C_2H_3O_2^-$. There are also present at the start 0.00134 gram-ion of hydrogen and 0.09866 gram-mole of non-ionized acetic acid. These quantities cannot exist together in these proportions without disturbing the equilibrium, since the ionization constant, 0.0000182, must be satisfied. The only way in which equilibrium can be restored is for acetate ions to combine with an equal number of hydrogen ions and form non-ionized acetic acid until the ratio again satisfies the equilibrium constant.

The extent to which the hydrogen-ion concentration is thus lowered and the extent to which the ionization of the acid is repressed are shown by the following calculation. Let x equal the amount by which the H^+ and $C_2H_3O_2^-$ concentrations are decreased and the $HC_2H_3O_2$ concentration increased. Substituting in the

equilibrium expression:

$$\frac{(0.00134 - x) \times (0.08134 - x)}{(0.09866 + x)} = 0.0000182$$

and solving, give for x a value of 0.00132, the amount by which the hydrogen- and acetate-ion concentrations are decreased and the concentration of non-ionized acetic acid is increased. The new hydrogen-ion concentration is therefore $0.00134 - 0.00132 = 0.00002$ gram-ion per liter showing a greatly decreased acidity.

By making certain approximations we can avoid the above quadratic equation. Let y stand for the final hydrogen-ion concentration. Assume that the final acetate-ion concentration is that resulting from the added $NaC_2H_3O_2$ and the final concentration of non-ionized $HC_2H_3O_2$ is the same as the molarity of the acetic acid. These assumptions are warranted since it can be seen from the above that the deviation from the exact amounts (x in the above calculation) is negligible. We have then:

$$\frac{y \times (0.1 \times 0.80)}{0.1} = 0.0000182$$

Solving this equation we have:

$$y = 0.0000227 \text{ gram-ion per liter}$$

which is the new H^+ concentration.

Just as an increase of acetate ions will lower the concentration of hydrogen ions which can exist in equilibrium with acetic acid, an increase in hydrogen ions from a strong acid will lower the acetate-ion concentration and repress the ionization of the acetic acid. Moreover, if a strongly ionized acid, such as HCl, is added to a solution of an acetate, the hydrogen ions together with acetate ions will be used up in forming non-ionized acetic acid. A strongly ionized acid will, in most cases, displace a weaker acid from its salts, owing to the repression of the ionization of the less ionized acid.

Buffer Solutions. By means of common-ion effect it is thus possible to lower and keep in control the concentration of certain ions. If the hydrogen-ion concentration, i.e., the acidity, of a solution is to be controlled, a weakly ionized acid, such as acetic or formic, is employed together with a salt of the acid, as for example sodium acetate or sodium formate. If the basicity, i.e., the OH^-

ion concentration, is to be controlled, NH_4OH and NH_4Cl are used A reagent thus prepared by mixing a weakly ionized acid or base with a salt of the acid or base, for the purpose of keeping within narrow limits the acidity or basicity of a solution, is known as a buffer solution. The solution is said to be "buffered." Common-ion effect on the equilibrium of the weak electrolyte is the basis of buffer action.

Important examples of buffer action are found in analytical procedures. In the schemes of qualitative analysis, use is made of buffer action in connection with the precipitation or non-precipitation of sulfides, of $Mg(OH)_2$ and a number of other substances. In the precipitation of the sulfides, the theory of which is discussed in detail on page 168, the sulfide-ion concentration is controlled by common-ion effect through the use of HCl, which furnishes a high H^+ concentration in common with the H^+ derived from the weakly ionized H_2S.

REVIEW EXERCISES — SET 4

1. What is an ionization constant? When the equilibrium law is applied to ionization, will the calculated values for the ratio vary with dilution for strong electrolytes? For weak electrolytes?

2. Calculate the equilibrium ratios for the different molarities of HCl given in Table II. Does the equilibrium law hold for dissolved electrolytes of this type?

3. What is the effect of dilution upon the degree of dissociation of a weak electrolyte? Explain. why

4. From the data for formic acid, $HCHO_2$, in Table II, calculate the ionization constant of this acid. Check the result with the value given in Table V.

5. The ionization constant for NH_4OH is 1.75×10^{-5}. What is the OH^- ion concentration in a 0.01 molar solution of this base?

6. Define a buffer solution. In general, how are such solutions prepared? Illustrate your answer with suitable examples.

7. To 500 ml. of 0.1 molar acetic acid solution are added 10 grams of sodium acetate. Assuming complete ionization of the salt, calculate the resultant hydrogen-ion concentration.

8. If 3.65 grams of HCl are added to a liter of water containing 3.4 grams of H_2S, what are the concentrations of H^+ ion and sulfide ion? $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$.

9. In order to establish $S^=$ ion concentrations of the following order of magnitude in solutions saturated with H_2S, what must be the corresponding H^+ ion concentrations? $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$.

$C_{S^-} =$ (a) 1×10^{-15}. (b) 1×10^{-17}. (c) 1×10^{-19}. (d) 1×10^{-21}.

10. If 4.9 grams of NaCN are added to a liter of 0.1 *M* HCN, what are the resulting concentrations of H^+ ion and CN^- ion? Assume 85 per cent ionization of the NaCN.

THE EQUILIBRIUM LAW APPLIED TO PRECIPITATION: THE SOLUBILITY PRODUCT PRINCIPLE

The equilibrium conditions existing in solutions in which precipitates are formed are extremely important inasmuch as most of the separations and tests of qualitative analysis involve either the formation or the dissolving of precipitates. It is therefore imperative to know which conditions lead to the formation of a precipitate and what changes take place when a precipitate dissolves. This application of the equilibrium law is known as the **solubility product principle.** In the following paragraphs we will first derive the relationship, then show how the special equilibrium constants, which characterize the equilibrium in such solutions, are calculated and finally apply the principle to the formation and dissolving of precipitates.

Formulation of the Solubility Product Equation. The solubility product principle states that, in a saturated solution of a difficultly soluble salt, the product of the gram-ion concentrations has a definite numerical value. In the case of the salt *AB*, whose ions are A^+ and B^-, the relationship, when equilibrium is reached, is expressed by the equation:

$$C_{A^+} \times C_{B^-} = K_{\text{s.p.}}$$

where $K_{\text{s.p.}}$ is a constant called the solubility product constant and is characteristic of the salt *AB*.

This relationship can be deduced in the following manner by using AgCl as a typical example and following the derivation proposed by Butler (*Chemistry and Industry*, **43,** 634 [1924], and *Jour. Phys. Chem.*, **28,** 438 [1924]). In a saturated solution of silver chloride containing an excess of the solid phase an equilibrium exists between the rate at which the solid dissolves and at which solid forms. The solid surface may be considered as a lattice of which a portion, x, contains exposed silver ions, the remaining surface $(1 - x)$ having chloride ions exposed. Considering the reversible action to take place separately for Ag^+ ions and for Cl^- ions, the rate at which Ag^+ ions leave the surface may be expressed by k_1x, in which k_1 is a proportionality factor (a velocity constant),

and the rate at which Ag^+ ions are deposited on the surface may be expressed by the formula $k_2(1 - x)C_{Ag^+}$, since the frequency of deposition will depend upon the concentration, C_{Ag^+}, of the Ag^+ ions in solution, as well as upon the area $(1 - x)$ having exposed chloride ions. At equilibrium the rates of detachment and of attachment of Ag^+ ions are equal and

$$k_1 x = k_2(1 - x)C_{Ag^+} \tag{1}$$

Likewise, the passing of Cl^- ions into solution may be expressed by $k_3(1 - x)$, and the deposition of Cl^- ions on the surface by $k_4 x C_{Cl^-}$; accordingly, at equilibrium

$$k_3(1 - x) = k_4 x C_{Cl^-} \tag{2}$$

From equation (1) the concentration of silver ion in solution is

$$C_{Ag^+} = \frac{k_1 x}{k_2(1 - x)}$$

and from (2)

$$C_{Cl^-} = \frac{k_3(1 - x)}{k_4 x}$$

For the combined action, we have then

$$C_{Ag^+} \times C_{Cl^-} = \frac{k_1 k_3}{k_2 k_4} = K_{s.p.}$$

It should be observed that no numerical or other factor appears for the amount of solid which may be present, an obvious result since, however much solid may be present, it will have no influence on the concentration of ions in a saturated solution.

This new constant, $K_{s.p.}$, is called the solubility product constant. It is a special equilibrium constant, relating to the equilibrium of the ions in a saturated solution. It can be used rigorously only for solutions formed from difficultly soluble compounds and in solutions of the pure salt. The expression means that, in a solution containing ions which by their union produce a difficultly soluble compound, the ions will be in equilibrium when the product of their gram-ion concentrations attains a certain definite, small value called the solubility product constant. When this constant is reached the solution is saturated with respect to the ions which form the solid. The constant has a different numerical value for each compound and varies with the temperature for the same

compound. It does not strictly apply to solutions containing ions derived from other salts, but holds good over a limited range only for solutions of a pure salt.

If the value for the constant is exceeded, the excess ions will separate out as a solid compound (a precipitate). In any solution in which there is undissolved solid, no matter how little or how much, the liquid surrounding the solid will always contain enough of the ions to make the product of their gram-ion concentrations equal to the constant characteristic for that particular solid. This ion relationship, as already noted, holds only for relatively insoluble compounds.

Calculation of Solubility Product Constants. Solubility product constants have been determined for practically all the compounds which are obtained as precipitates in analytical work. They can be calculated from the solubility data. The solubility in grams per liter, determined by experiment, is converted into the molar solubility by dividing by the molecular weight of the dissolved compound. From this the concentration of each set of ions may be calculated. If it is known that the ionization of the dissolved solute is not complete, the molar solubility is multiplied by the per cent to which the solution ionizes. For example, the solubility of AgCl at room temperature is 0.0015 gram per liter. Dividing this by the molecular weight of AgCl, 143.34, gives 0.0000106 gram-mole, which is the molar concentration of the dissolved AgCl. This is an extremely dilute solution and the AgCl is assumed to be completely ionized. This liter of solution therefore contains 0.0000106 or 1.06×10^{-5} gram-ion of Ag^+ ion and the same concentration of Cl^- ion.

The solubility product equation is:

$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.}$$

and substituting the numerical values for the concentrations we have:

$$(1.06 \times 10^{-5}) \times (1.06 \times 10^{-5}) = 1.1 \times 10^{-10}$$

giving 1.1×10^{-10} as the $K_{s.p.}$ of AgCl.

Where three different sets of ions are formed from a dissolved solid, the product of the gram-ion concentration of all three sets is the desired $K_{s.p.}$ In the case of $MgNH_4PO_4$, the precipitate involved in the tests for magnesium and phosphate ions, the

solubility is 0.0086 gram per liter or a molar solubility of 6.3×10^{-5}. The ionization of this compound takes place according to the equation:

$$MgNH_4PO_4 \rightleftharpoons Mg^{++} + NH_4^{+} + PO_4^{\equiv}$$

The gram-ion concentrations, therefore, in a saturated solution, assuming complete ionization, are 6.3×10^{-5} for each set of ions. The $K_{s.p.}$ is then:

$$\begin{array}{ccccccc} C_{Mg^{++}} & \times & C_{NH_4^+} & \times & C_{PO_4^{\equiv}} & = & K_{s.p.(MgNH_4PO_4)} \\ (6.3 \times 10^{-5}) & \times & (6.3 \times 10^{-5}) & \times & (6.3 \times 10^{-5}) & = & 2.5 \times 10^{-13} \end{array}$$

If the dissolved solid yields three ions, two of which are alike, the total gram-ion concentration of each set of ions must be determined from the molar solubility of the dissolved solute; after this the total concentration is squared for that set which appears twice into the equation. This may be made clear in the case of $Mg(OH)_2$. This substance is ionized according to the equation:

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + OH^- + OH^-$$

yielding one magnesium ion and two hydroxyl ions for each molecule ionized. The equilibrium expression is therefore:

$$C_{Mg^{++}} \times C_{OH^-} \times C_{OH^-} = K_{s.p.}$$

or

$$C_{Mg^{++}} \times (C_{OH^-})^2 = K_{s.p.}$$

The molar solubility of $Mg(OH)_2$ at room temperature is 0.000206; hence, the concentration of Mg^{++} is 0.000206 gram-ion per liter and the concentration of the hydroxyl ion is twice as great, or 0.000412 gram-ion per liter. The value of the constant is therefore:

$$\begin{array}{ccccc} C_{Mg^{++}} & \times & (C_{OH^-})^2 & = & K_{s.p.(Mg(OH)_2)} \\ (0.000206) & \times & (0.000412)^2 & = & 3.5 \times 10^{-11} \end{array}$$

Confusion in calculations involving solubility product relationships will be avoided if it is always remembered (1) to use the *total* concentration of each set of ions and (2) to square or cube this total concentration according to whether the particular set is involved two or three times in the ionization equation. Note particularly in the above example that *we did not double* the hydroxyl-ion concentration; we simply doubled the concentration

of the dissolved $Mg(OH)_2$ or of the Mg^{++} *in order to find* the concentration of the OH^-. This point is emphasized because it is the source of more difficulty than any other factor involved in solubility-product calculations.

Solubility product constants of a number of slightly soluble substances are given in Table VI, for which the data were collected from various sources. Most of these results have been calculated from the electrical conductivity of the saturated solutions. Because of the experimental difficulties encountered in the measure-

TABLE VI

SOLUBILITY PRODUCT CONSTANTS

Compound	$K_{s.p.}$	Compound	$K_{s.p.}$
$AgCl$	1.1×10^{-10}	SrC_2O_4	5×10^{-8}
$AgBr$	3.5×10^{-13}	CaC_2O_4	2.6×10^{-9}
AgI	1.0×10^{-16}	$SrSO_4$	3.5×10^{-7}
Hg_2Cl_2	2.0×10^{-18}	$BaSO_4$	1.2×10^{-10}
$PbCrO_4$	1.7×10^{-14}	$CaSO_4$	2.2×10^{-4}
$PbSO_4$	2.3×10^{-8}	HgS	4.1×10^{-53}
$PbCl_2$	2.4×10^{-4}	CuS	8.5×10^{-45}
$Fe(OH)_3$	1.1×10^{-36}	CdS	3.6×10^{-29}
$Mg(OH)_2$	3.5×10^{-11}	PbS	4.0×10^{-28}
$MgNH_4PO_4$	2.5×10^{-13}	ZnS	1.2×10^{-23}
$MgCO_3$	4.2×10^{-5}	FeS	1.5×10^{-19}
$CaCO_3$	4.8×10^{-9}	MnS	1.4×10^{-15}
$SrCO_3$	1.6×10^{-9}		
$BaCO_3$	7.0×10^{-9}		
$BaCrO_4$	2.3×10^{-10}		

ments the solubility product constants of many compounds are so uncertain as to be practically valueless. This is true especially of most hydroxides and many sulfides and for this reason values for many of these compounds are omitted from the table. Also, different values for the same constant are given by different investigators; those included here are believed to be the most reliable.

The solubility product constant, like the solubility, changes with the temperature. The values here given apply with reasonable accuracy to solutions at ordinary room temperatures. Room temperature is assumed in all of the following problems involving solubility product constants.

Application of the Solubility Product Principle to Precipitation. The solubility product constant gives a measure of the concentration of ions which are in equilibrium in a saturated solution of a sparingly soluble electrolyte. This value must be reached to establish equilibrium and must be exceeded before a solid, i.e. a precipitate, will separate out. Since the constant is a *product* of two or more factors expressing concentration of ions in equilibrium, these concentrations need not necessarily be equivalent to each other, as was the case in calculating the constants from pure solutions of the compound; all that is required for equilibrium to be established is for the *product* of the gram-ion concentrations to reach the numerical value of the constant for the compound in question.

What happens during the formation of a precipitate is this: Precipitating ions are added, in the form of a solution of an electrolyte, to the solution which contains the ions to be precipitated. When an amount of precipitating ions is added such that the product of the ion concentrations (the gram-ion concentration of precipitating ions $\times$ gram-ion concentration of ions to be precipitated) is exactly equal to the $K_{s.p.}$, the ions will be in equilibrium and the solution will be saturated. Addition of a further amount of precipitating reagent will result in the formation of a precipitate, since the solution is already saturated with ions. The solid will continue to separate during the addition of precipitating ions until the ions whose precipitation is desired have been practically, but not entirely, removed from solution. At all times after a precipitate has initially formed, the solution surrounding it contains the two or more sets of ions in such amounts that the product of their gram-ion concentrations always equals the solubility product constant.

Before considering further the extent to which it is possible to remove ions by precipitation, let us apply the principle to the formation of a precipitate of AgCl. Suppose it is desired to make a qualitative test for silver in a solution of $AgNO_3$ which is 0.0001 *M*. At this dilution the solution is practically completely ionized so that the gram-ion concentration of silver ion is 0.0001. The quantity of chloride ion required before a precipitate of AgCl will form can be readily calculated from the $K_{s.p.}$ expression:

$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.(AgCl)}$$
$$0.0001 \times x = 1.1 \times 10^{-10}$$

from which $x = 0.000001$ gram-ion of Cl^-, the amount which must be added in the form of HCl, NaCl or any other soluble chloride in order to saturate the solution. Any amount beyond this will result in a precipitate of AgCl and give the desired test for silver. As more and more chloride ions are added they will at once unite with silver ions, precipitating increasing quantities of AgCl and progressively lowering the concentration of silver ions remaining in solution.

Effect of Excess Precipitating Agent. As long as AgCl continues to form, silver ions and chloride ions are being removed in equal quantities, and to satisfy the equilibrium requirements the supply of ions must be maintained by adding more chloride ions. A point is eventually reached when the concentration of chloride ions is greatly in excess of silver ions but still equilibrium is maintained. What is required therefore to cause the reaction to run practically to completion and to insure almost complete precipitation (and separation) is the addition of an excess of precipitating ions. An excess of precipitating agent will have the effect of forcing more of the solid to separate out; this is analogous to the effect of a large excess of common ions in repressing the ionization of weak electrolytes. The effect on the equilibrium in both cases is to lower the concentration of the other set of ions.

In following the course of ionic changes during precipitation we must recognize two stages, namely, first, the stage at which equilibrium is first established when the $K_{s.p.}$ is reached and beyond which precipitation will take place; second, the final stage, in which the concentration of precipitating ion is greatly in excess of that for the ions whose (practical) complete removal is desired. At all times after the first stage, the product of the concentrations is numerically equal to the $K_{s.p.}$ of the compound being precipitated. Absolutely complete removal of ions is, according to this principle, impossible, but for practical purposes of separation the precipitation is sufficiently complete.

Application of the Solubility Product Principle to the Dissolving of Precipitates. Inasmuch as the solution surrounding any precipitate is saturated with respect to the ions which form that precipitate, the ions are in equilibrium with each other. If the concentration of one or the other or both ions is lowered the equilibrium will be disturbed and more solid will dissolve in order to restore equilibrium. Thus, increasing the amount of solvent will lower

the concentration of both ions and more solid will dissolve at the greater dilution; or the addition of a reagent which will cause a decrease in ionization, by forming, for example, a weakly ionized electrolyte or a complex ion, will disturb the equilibrium and remove ions from solution. For example, calcium oxalate will dissolve in dilute HCl. This is explained as follows.

When HCl is added to CaC_2O_4 the equilibria shown below are set up:

$$CaC_2O_4 \rightleftharpoons Ca^{++} + C_2O_4^{=}$$

$$\begin{array}{cccc} 2HCl \rightleftharpoons & 2Cl^- & + & 2H^+ \\ \text{(highly ionized)} & \updownarrow & & \updownarrow \\ & CaCl_2 & & H_2C_2O_4 \\ & \text{(highly ionized)} & & \text{(less ionized than HCl)} \end{array}$$

The $C_2O_4^{=}$ ions in equilibrium with Ca^{++} ions are used up in forming oxalic acid, thus disturbing the equilibrium, and in order to restore it more solid CaC_2O_4 must dissolve and ionize. Final equilibrium will be established when all the solid CaC_2O_4 has dissolved.

Another example, the dissolving of ZnS in HCl, may be cited. The ionic changes and the equilibria finally established may be diagrammed thus:

$$ZnS \rightleftharpoons Zn^{++} + S^{=}$$

$$\begin{array}{cccc} 2HCl \rightleftharpoons & 2Cl^- & + & 2H^+ \\ & \updownarrow & & \updownarrow \\ & ZnCl_2 & + & H_2S \\ & \text{(highly ionized)} & & \text{(weakly ionized)} \end{array}$$

The formation of weakly ionized H_2S which, being slightly soluble, escapes from the solution, lowers the sulfide-ion concentration; to maintain the equilibrium between sulfide ions and zinc ions, demanded by the $K_{s.p.}$, more solid ZnS must dissolve. Final equilibrium will be attained only when all the ZnS has dissolved.

The formation of complex ions as a means of disturbing equilibrium will be discussed on page 79.

Fractional Precipitation. The foregoing discussion of the theory of precipitation has considered the simple case of a single precipitate being formed. The situation is more complicated where two or more kinds of ions are present in the same solution, each set

capable of being precipitated by the same reagent. The questions arise: Which set will be precipitated first, and will the first set be completely precipitated before the second set begins to react with the precipitant?

Obviously, when a precipitating ion is added to a solution containing two kinds of ions, each of which can form an insoluble compound with the added ion, the solution will become saturated with respect to the less soluble compound before it becomes saturated with respect to the more soluble compound. For example, a solution containing equal concentrations of Br^- and Cl^- will become saturated, when silver ions are added, with respect to Ag^+ and Br^- before the saturation value for Ag^+ and Cl^- is reached, because the $K_{s.p.}$ of AgBr is smaller than that of AgCl. Consequently, AgBr will begin to precipitate first. Upon the continued addition of Ag^+ the $K_{s.p.}$ of AgCl will eventually be reached and both AgBr and AgCl will be precipitated simultaneously. The concentrations of Br^- and Cl^- then bear a constant ratio to each other, as can be shown in the following way:

$$C_{Ag^+} = \frac{K_{s.p.(AgCl)}}{C_{Cl^-}} = \frac{K_{s.p.(AgBr)}}{C_{Br^-}}$$

from which

$$\frac{C_{Cl^-}}{C_{Br^-}} = \frac{K_{s.p.(AgCl)}}{K_{s.p.(AgBr)}} = \frac{1.1 \times 10^{-10}}{3.5 \times 10^{-13}} = 0.31 \times 10^3 = 310$$

Hence, in a solution that is saturated with both AgCl and AgBr there will be approximately three hundred times as many chloride ions as bromide ions. In any event, the ratio will be the same as the ratio of the solubility product constants of the two compounds. Such a partial precipitation of one substance in the presence of a less soluble substance having an ion in common with the first is termed **fractional precipitation.** It is involved whenever two or more compounds are precipitated from the same solution by the same reagent.

The Properties of Precipitates

The solubility product principle, valuable as it is, does not tell the whole story of precipitation. In fact, there are so many factors of which it takes no account that its application to many

experimentally encountered situations is quite unjustified. Some of these factors are so important that they cannot be disregarded.

The Salt Effect. We have seen that the addition of a common ion decreases the solubility of a precipitate. It might be inferred that the addition of an electrolyte having no common ion would have no effect on the solubility of the precipitate, but this is far from the truth. The presence of foreign ions *increases* the solubility of a slightly soluble compound, in some cases to an appreciable extent. For instance, a solution that is 0.01 M in KNO_3 will dissolve approximately twice as much $BaSO_4$ as is dissolved by pure water and a 0.5 M solution of NaCl will dissolve about five times as much CaC_2O_4 as pure water.

This effect of foreign ions on the solubility of a precipitate is called the salt effect. The effect increases with increase in the charge on the foreign ion and also with an increase in the charge on the ions of the precipitate. The foreign ions decrease the activity coefficients of the ions of the precipitate and this decrease must be counterbalanced by an increase in the concentrations of the ions. This can be shown in the following way, $BaSO_4$ being used as an example.

We have already pointed out (page 19) the fact that equilibrium expressions are rigidly true only if activities are used in place of concentrations. That is:

$$a_{Ba^{++}} \times a_{SO_4^{--}} = K_{s.p.}$$

But $$a_{Ba^{++}} = f_1C_{Ba^{++}};\ a_{SO_4^{--}} = f_2C_{SO_4^{--}}$$

where f is the activity coefficient. Therefore,

$$f_1C_{Ba^{++}} \times f_2C_{SO_4^{--}} = K_{s.p.}$$

is the more correct formulation of the solubility product expression for $BaSO_4$. If, now, the addition of foreign ions *decreases the activity coefficients f_1 and f_2*, it is obvious that in order to keep $K_{s.p.}$ unchanged the *concentrations $C_{Ba^{++}}$ and $C_{SO_4^{--}}$ must increase;* that is, more of the precipitate goes into solution.

It is not absolutely essential that the additional ions be foreign ions; an excess of a common ion will have a similar effect. This means that in order to secure maximum precipitation a great excess of the precipitating agent is to be avoided, because eventually the increase in solubility due to the salt effect more than balances the decrease due to the common-ion effect.

Complex-Ion Formation. In addition to the salt effect, another factor sometimes operates to increase the solubility of a precipitate in an excess of precipitating agent. As mentioned previously, AgCl, for instance, will dissolve completely in an excess of concentrated HCl, owing to the formation of complex ions of the type $AgCl_3^{=}$ or $AgCl_4^{\equiv}$. Any solution which furnishes a very high concentration of chloride ions will, of course, increase the solubility of AgCl. $PbCl_2$ acts similarly, forming $PbCl_4^{=}$.

We have considered here only those complex ions formed with an excess of the precipitating agent. It is, however, possible to form a large number of other complex ions; such a process is frequently used to produce separations in qualitative analysis. Thus, AgCl will dissolve readily in solutions of KCN, NH_3 or $Na_2S_2O_3$:

$$\underline{AgCl} + 2CN^- \rightleftharpoons Ag(CN)_2^- + Cl^-$$

$$\underline{AgCl} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$

$$\underline{2AgCl} + 3S_2O_3^{=} \rightleftharpoons Ag_2(S_2O_3)_3^{==} + 2Cl^-$$

The structure of certain ions of this type is discussed on page 81 and the equilibria relationships involved are considered on page 79.

Colloidal Systems. In a true solution the solute is present in particles of molecular or ionic size — about 10^{-8} cm. in diameter. If the solute particles are larger, but not so large that they settle out on standing for a reasonable length of time, they are said to be in the colloidal condition and the mixture is a colloidal system. The limits of size of colloidal particles may be placed arbitrarily at diameters of 10^{-4} and 10^{-7} cm.

For convenience liquid colloidal systems may be divided into two general classes — sols and gels — although there is no sharp distinction between the two. The terms suggest the general characteristics of the systems: sols are similar to solutions (low viscosity, filterable, etc.) and gels resemble jellies; in fact, jellies are gels. Although some compounds, such as the hydroxides of iron and aluminum, precipitate as gels, this type of colloidal system occurs less frequently in qualitative analysis.

Sols, however, are of considerable importance, primarily because of our desire to avoid them. The dispersed particles in sols cannot be removed by filtering and usually not by centri-

fuging for a reasonable length of time; consequently, sol formation may make an analytical separation incomplete or impossible. Sol formation is particularly undesirable in the semi-micro method because of the small amounts of materials used and the extreme sensitivity of some of the tests to contaminating ions.

The suspended particles in sols all carry either positive or negative electric charges; that is, sol particles are essentially gigantic ions. The charges arise in either of two general ways: (1) adsorption of ions from the solution onto the surface of the sol particle; (2) partial ionization of some component of the sol particle, the ions of one sign going into the solution and the ions of opposite sign remaining on the sol particle. Whatever the origin of the charges, they cause the sol particles to repel each other, thus tending to prevent collisions and consequent coagulation of the sol. The charges, then, stabilize the sol. If these charges can be removed or decreased sufficiently the sol particles will collide more frequently and coagulation will occur.

Heating tends to remove the adsorbed ions and hence encourages coagulation. If ions of charge opposite to that of the particle are adsorbed in sufficient numbers they will effectively neutralize the charge of the particle and consequently produce coagulation. Therefore, the addition of an ionized compound to the system will sometimes bring about precipitation of the sol.

An obvious objection to this method of precipitating a sol is the impossibility of adding negative ions to a positively charged sol without adding at the same time an equivalent number of positive ions. The latter might reasonably be expected to aid in stabilizing the sol and thus counteract the coagulating effect of the negative ions. The same argument holds, of course, for negative sols and positive coagulating ions. This stabilizing effect, although it undoubtedly exists, is, however, of less significance than the coagulating tendency of the oppositely charged ions.

A very important factor in determining the coagulating power of an ion is the number of units of charge that it carries. The coagulating ability increases greatly with increase in the charge. Thus, aluminum compounds are much more effective than magnesium compounds, which in turn are more effective than sodium compounds, in coagulating negative sols; similarly phosphates, sulfates and chlorides have decreasing abilities, in the order named, to coagulate positive sols.

As far as application in a scheme of analysis is concerned, however, this charge effect usually cannot be utilized because divalent and trivalent ions, if added, will almost always produce unwanted precipitations or other reactions. Hydrogen and hydroxyl ions are much more effective than other monovalent ions and are sometimes used to coagulate colloidal particles. NH_4NO_3 and NH_4Cl are the salts most commonly used to destroy colloidal suspensions because, although they are not as effective as other salts, they do not complicate the usual scheme of analysis. The addition of these compounds to the water used to wash precipitates tends to prevent the precipitate from going into the colloidal condition. Frequent use is made of this fact in the schemes of analysis.

Colloidal systems may be formed spontaneously in precipitations or in oxidation-reduction reactions, especially in those involving the formation or dissolving of sulfides. Thus, the addition of H_2S to a solution containing ions of a metal which forms a slightly soluble sulfide will frequently produce a colloidal suspension of the sulfide, especially if the solution is alkaline. The sulfide sol is stabilized by the adsorption of H_2S, hydrosulfide or sulfide ions (the latter two are present in high concentration in an alkaline solution) and may usually be coagulated by increasing the acidity of the system, provided, of course, the increased acidity does not cause the precipitate to redissolve. Similarly, the oxidation of H_2S or a sulfide or the acidification of a polysulfide usually results in the formation of a white colloidal suspension of sulfur which may be very hard to eliminate.

In the analytical scheme sulfur suspensions are almost invariably obtained (*a*) in precipitating Group II of the cations if any oxidizing agents are present, (*b*) in dissolving the Group II-A sulfides in HNO_3 and (*c*) in reprecipitating Group II-B sulfides by acidifying the polysulfide solution. When very strong oxidizing agents are used some of the sulfur is oxidized to $SO_4^=$ but it is difficult to eliminate all of it in this way.

Up to this point we have said less about gels than their importance merits. Gels and sols differ not in type but only in degree. Many compounds which easily form sols can be obtained in the form of gels by using appropriate techniques. For instance, $BaSO_4$ as usually precipitated forms a sol, but if saturated solutions of $Ba(CNS)_2$ and $MnSO_4$ (the most soluble barium salt and the most

soluble metallic sulfate) are mixed, a gel of $BaSO_4$ is obtained; this gel is so viscous that it cannot be poured from the container.

One of the factors determining whether a given precipitation process will result in the formation of a sol or a gel is the rate of formation of nuclei of the precipitate; if the rate of formation is very high a gel will result and if it is relatively low a sol will be formed. The rate of nuclei formation will be higher as the concentrations of the precipitating solutions are greater and as the solubility of the precipitate is lower. Consequently, gel formation may be minimized by carrying out precipitations slowly, at the boiling point, using solutions that are not too concentrated. These conditions discourage the formation of any type of colloidal system.

Some precipitates, however, are gelatinous even if all the above conditions are observed. Among these are the hydroxides of iron, aluminum and chromium. These form gels because their solubility is so exceedingly low that this factor outweighs all the others.

To speak of gelatinous precipitates in general and of the above hydroxides in particular as definite chemical compounds is a type of chemical fiction. It is doubtful whether a compound such as, for example, $Fe(OH)_3$ actually exists; if it does, it is not the reddish, gelatinous material to which this formula is usually applied. The so-called ferric hydroxide is really a hydrated oxide of indefinite composition, perhaps best represented by the formula $Fe_2O_3(H_2O)_x$, or possibly by FeOOH. The same is true of most " hydroxides " of trivalent and tetravalent metals, so when the student encounters such formulas as $Al(OH)_3$ and $Mn(OH)_4$ he should interpret them as meaning " hydrated Al_2O_3 " and " hydrated MnO_2."

Contamination of Precipitates. When any precipitate separates from a solution it carries with it from the solution, either occluded within the crystals or adsorbed on the surface, some of the cations and anions which normally constitute soluble compounds. Thus, if AgCl is precipitated from solutions of $AgNO_3$ and NaCl, the precipitate, even after washing, will contain some NaCl. This phenomenon is called **coprecipitation.** The soluble coprecipitated compound very frequently has one ion in common with the precipitate.

If the foreign substance is not carried down along with the main precipitate but forms later on the surface of the precipitated par-

ticles it is said to be postprecipitated; this phenomenon is called **postprecipitation.** This effect is noticed particularly with the sulfides. Zinc, for instance, will not precipitate as ZnS when a 0.01 *M* solution of a zinc salt, 0.1 *M* in hydrogen ion, is saturated with H_2S, even though the solution is supersaturated with ZnS. If, however, Hg^{++}, Cu^{++} or some other metallic ion which forms a very insoluble sulfide is present, this sulfide will precipitate immediately when H_2S is added and ZnS will then be precipitated from the supersaturated solution onto the surface of the other sulfide. In this way as much as 95 per cent of the zinc in a solution may be postprecipitated on another sulfide under conditions such that if the second sulfide were not present no ZnS would appear.

In schemes of qualitative analysis which utilize H_2S to precipitate Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, etc., from acid solution, a large proportion of any Zn^{++} present may be postprecipitated on these sulfides and therefore lost. This may account for the difficulty that is sometimes experienced in detecting zinc at its proper place in the scheme of analysis.

It is to be noted that the failure of ZnS to precipitate when H_2S is passed into a moderately acid solution of a zinc salt is due not to its solubility but, apparently, to the slowness of the reaction and to the formation of a highly supersaturated solution of ZnS. The presence of other sulfides does not render the ZnS less soluble but simply promotes precipitation from an already supersaturated solution.

It must not be supposed that postprecipitation is limited to zinc sulfide or even to sulfides in general. The only requirement for postprecipitation is that the solution be supersaturated with respect to some constituent which normally would not be precipitated because of the slowness of crystallization. This condition is satisfied much too frequently in qualitative analysis.

Contamination is especially high for those precipitates which are obtained in a gelatinous form, such as the hydrated oxides of iron and aluminum. Much of the contamination is due to the large amount of mother liquor included in the precipitate; this can be removed by repeated washing. There is, however, an appreciable amount of adsorbed contaminants which cannot be removed by washing.

REVIEW EXERCISES — SET 5

1. Calculate the solubility product constants of the following salts, assuming complete ionization:

Salt	*Solubility Moles per Liter*
(*a*) $BaSO_4$	1.1×10^{-5}
(*b*) $Zn(OH)_2$	6.3×10^{-7}
(*c*) Hg_2Cl_2	8.0×10^{-7}
(*d*) $BaCrO_4$	1.5×10^{-5}
(*e*) ZnS	3.5×10^{-12}

2. Calculate the solubility product constants of the following salts, given the solubility in grams per liter and assuming complete ionization:

Salt	*Solubility Grams per Liter*
(*a*) HgS	1.5×10^{-24}
(*b*) MnS	3.3×10^{-6}
(*c*) $Mg(OH)_2$	1.2×10^{-2}
(*d*) Hg_2I_2	2.0×10^{-7}
(*e*) $Fe(OH)_3$	4.8×10^{-8}

3. Calculate the chloride-ion concentration necessary just to start the precipitation of the chlorides of Group I, in the test solutions of Ag^+, Pb^{++} and Hg_2^{++}, each solution containing 10 milligrams of the ion per milliliter (10 grams per liter).

Solution	$K_{s.p.}$
(*a*) Ag^+	1.1×10^{-10}
(*b*) Pb^{++}	2.4×10^{-4}
(*c*) Hg_2^{++}	2.0×10^{-18}

4. Calculate the gram-ion concentration of Fe^{+++} required to produce a precipitate of $Fe(OH)_3$ in a liter of ammonium hydroxide which contains 1×10^{-4} gram-ion of OH^-. The $K_{s.p.}$ of $Fe(OH)_3$ is 1.1×10^{-36}.

5. The Mg^{++} test solution contains 10 milligrams Mg^{++} ion in each milliliter. What OH^- ion concentration is required to cause precipitation of $Mg(OH)_2$ in such a solution? The $K_{s.p.}$ of $Mg(OH)_2 = 3.5 \times 10^{-11}$.

6. At what hydrogen-ion concentration will MnS just begin to precipitate when H_2S is passed into a solution that is 0.10 *M* in Mn^{++}?

7. CaC_2O_4 is soluble in HCl but not in $HC_2H_3O_2$. Explain fully why this is to be expected?

8. What is the maximum amount of Na_2SO_4 that can be added to 1 ml. of a solution containing 1 milligram of Sr^{++} without causing precipitation or supersaturation?

9. What is a colloidal system? What are the limits of size of the particles in a solid-liquid system? What is a sol? A gel? How may each be formed? Why are colloidal systems undesirable, in general, in analytical

chemistry? Can you think of any that are desirable in analytical chemistry? How may the formation of sols be avoided? How may sols be coagulated?

10. Define coprecipitation and postprecipitation. Why are these effects of particular importance in analytical chemistry?

THE THEORY OF COMPLEX IONS

The Composition of Ions. Ions differ greatly in their chemical composition, as well as in the nature and number of their electrical charges. The simplest ions consist of charged atoms; for example, the positively charged metal atoms such as Ag^+, Cu^{++}, Cd^{++}, Fe^{++} and Fe^{+++}, and the negatively charged atoms of non-metallic elements such as the sulfide ion, $S^=$, and the halide ions, F^-, Cl^-, Br^-, I^-. On the other hand, atoms of different elements may unite into radicals, which, when charged, form ions of widely varying molecular complexity. Among these charged groups of atoms are many which in their chemical reactions behave as simple ions, as, for example, the ammonium cation, NH_4^+, and such acid radicals as the cyanide, CN^-, the sulfate, $SO_4^=$, the arsenate, $AsO_4^{\equiv}$, and the tartrate, $C_4H_4O_6^=$, anions. There is yet another considerable group of ions of still greater complexity whose reactions and equilibrium relationships are extremely important in analytical procedures. To this latter group the term " complex ions " is applied.

Complex Ions. The most important complex ions encountered in qualitative analysis are those formed by the combination of metal ions with (*a*) ammonia and (*b*) cyanide ions, (*c*) sulfide ions, (*d*) halide ions and (*e*) organic ions. Examples of these complexes are discussed below.

Complex Ions of Metals with Ammonia. Silver chloride dissolves in ammonium hydroxide (an aqueous solution of NH_3) according to the reaction:

$$AgCl + 2NH_3 = Ag(NH_3)_2^+ + Cl \qquad (1)$$

The complex diammono-silver ions further ionize to a very slight extent into Ag^+ ion and $2NH_3$:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \qquad (2)$$

The equilibrium expression for reaction (2) is:

$$\frac{C_{Ag^+} \times (C_{NH_3})^2}{C_{Ag(NH_3)_2^+}} = K$$

The equilibrium constant, K, is called the instability constant of the complex $Ag(NH_3)_2^+$ ion. Its value is 7×10^{-8}. This small value of K shows that the complex ion is relatively very stable and that, in an ammoniacal solution of a silver salt, the silver is very largely combined with NH_3 and exists mainly as the complex $Ag(NH_3)_2^+$ ion.

Other similar complex ions of considerable importance in qualitative analysis are those of copper, $Cu(NH_3)_4^{++}$; of cadmium, $Cd(NH_3)_4^{++}$; of nickel, $Ni(NH_3)_4^{++}$; of cobalt, $Co(NH_3)_4^{++}$, and of zinc, $Zn(NH_3)_4^{++}$.

Complex Metal-Cyanide Ions. A number of metallic ions form complex ions with the cyanide ion. The best known of these are the ferrocyanide ion, $Fe(CN)_6^{\equiv\equiv}$, and the ferricyanide ion, $Fe(CN)_6^{\equiv}$, which in the form of potassium salts are used as test reagents for iron and certain other metals. Other complex cyanide ions are: the cuprous cyanide, $Cu(CN)_4^{\equiv}$; the cadmium cyanide, $Cd(CN)_4^{=}$; the silver cyanides, $Ag(CN)_2^-$ and $Ag(CN)_3^{=}$, and those of mercury, nickel, cobalt and gold, viz., $Hg(CN)_4^{=}$, $Ni(CN)_4^{=}$, $Co(CN)_6^{\equiv}$ and $Au(CN)_2^-$.

Complex Metal-Sulfide Ions. When ammonium sulfide, $(NH_4)_2S$ (the so-called colorless, monosulfide reagent), acts on As_2S_3, the precipitated arsenious sulfide dissolves forming the ion $AsS_3^{\equiv}$, called the thioarsenite or sulfoarsenite ion:

$$\underline{As_2S_3} + 3S^{=} = 2AsS_3^{\equiv}$$

The equilibrium here may be formulated by the equation:

$$\frac{(C_{As^{+++}}) \times (C_{S^=})^3}{C_{AsS_3^{\equiv}}} = K_{(\text{instability})}$$

Similar equilibria may be formulated for the $AsS_4^{\equiv}$, $SbS_3^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^{=}$ and $HgS_2^{=}$ complex ions. Since these complexes are very stable, the instability constants are very small numbers. The constants for many complex ions have not been determined. Knox (Trans. Faraday Soc., 4, 36, 1908) has determined the value for the ratio $C_{Hg^{++}} \times (C_{S^=})^2 \div C_{HgS_2^=}$ to be 1×10^{-53}.

These complex metal-sulfide ions are analogous to the better known oxy-ions of these elements. In fact, in composition they may be regarded as the oxy-ions (acid radicals) in which the oxygen has been replaced by sulfur. The analogy is shown in the following tabulation:

Oxy–Ions		Thio–Ions	
Arsenite	$AsO_3^{\equiv}$	Thioarsenite	$AsS_3^{\equiv}$
Arsenate	$AsO_4^{\equiv}$	Thioarsenate	$AsS_4^{\equiv}$
Antimonite	$SbO_3^{\equiv}$	Thioantimonite	$SbS_3^{\equiv}$
Antimonate	$SbO_4^{\equiv}$	Thioantimonate	$SbS_4^{\equiv}$
Stannite	$SnO_2^{=}$	Thiostannate	$SnS_3^{=}$
Stannate	$SnO_3^{=}$		

Other Complex Ions. Certain metal ions readily form complex ions with halide ions. Mercury, for example, forms the complex chloride, bromide and iodide ions, viz., $HgCl_4^{=}$, $HgBr_4^{=}$, $HgI_4^{=}$. The instability constants for these are given in Table VII. In the familiar precipitating agent for potassium, H_2PtCl_6, the platinum forms the complex chloroplatinate ion, $PtCl_6^{=}$, with the chloride ion. Gold also forms complex halide ions. These complexes are of considerable importance in analytical procedures.

TABLE VII

Instability Constants at 25° C.

Dissociation Reaction	$K_{\text{instability}}$
$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2NH_3$	7×10^{-8}
$Ag(CN)_2^- \rightleftarrows Ag^+ + 2CN^-$	1×10^{-21}
$NH_4^+ \rightleftarrows H^+ + NH_3$	6×10^{-10}
$Cu(NH_3)_4^{++} \rightleftarrows Cu^{++} + 4NH_3$	1×10^{-7}
$Cu(CN)_4^{\equiv} \rightleftarrows Cu^+ + 4CN^-$	5×10^{-28}
$Cd(NH_3)_4^{++} \rightleftarrows Cd^{++} + 4NH_3$	1×10^{-7}
$HgCl_4^{=} \rightleftarrows Hg^{++} + 4Cl^-$	1×10^{-16}
$HgBr_4^{=} \rightleftarrows Hg^{++} + 4Br^-$	2×10^{-22}
$HgI_4^{=} \rightleftarrows Hg^{++} + 4I^-$	5×10^{-31}
$Hg(CN)_4^{=} \rightleftarrows Hg^{++} + 4CN^-$	4×10^{-41}
$Zn(NH_3)_4^{++} \rightleftarrows Zn^{++} + 4NH_3$	3×10^{-10}

Complexes also form between certain metallic ions and organic radicals. The tartrate ion, in particular, has the tendency to combine with metals such as copper and antimony, thereby interfering with tests for these metallic ions.

The Structure of Complex Ions. Covalence, and coordinate valence, especially, are important in the discussion of complex ions because it is by means of these two types of bonds that the parts of a complex ion are held together. To get some idea of the nature of this binding we may use for a simple example the intensely blue complex ion formed by adding a solution of NH_3 to a solution of a

copper salt, a reaction with which the student is undoubtedly familiar. The copper ion as it exists in the original solution has, of course, no electrons in the valence shell. The nitrogen atom in NH_3 has shared 3 of its 5 electrons with 3 hydrogen atoms, giving it a total of 8 electrons in its valence shell and leaving a pair of electrons not shared with any atom. The NH_3 molecule accordingly shares this pair of electrons with the Cu^{++} ion; a similar action on the part of 3 other NH_3 molecules gives the ion a stable group of 8 electrons in its valence shell while still retaining its original charge. The condition in which the ion has a valence group of 8 electrons appears to be a more stable arrangement than that in which the valence group is entirely empty, so that the complex ion is a relatively stable ion. We may represent the complex ion as follows:

$$\left[\begin{array}{c} NH_3 \\ \downarrow \\ H_3N \rightarrow Cu \leftarrow NH_3 \\ \uparrow \\ NH_3 \end{array}\right]^{++}$$

The NH_3 molecule when combined in a complex ion is called the ammono group, so this ion is properly called the tetrammonocupric ion.

A statement similar to the above may serve to explain the structures of very many complex ions and hydrates, the latter being, at least in many instances, a type of complex ion. A difficulty arises in cases like $Ag(NH_3)_2^+$ and $Co(NH_3)_6^{+++}$ where, following the same general line of thought, it would appear that there are, respectively, 2 and 6 coordinate bonds and hence 4 and 12 electrons in the valence groups of the silver and cobalt, whereas we have been led always to expect a stable group of 8. This difficulty may be resolved, but not without damage to the apparent simplicity of the preceding discussion, by assuming (1) that the stable group need not always consist of 8 electrons but may at times, depending largely upon the relative sizes of the atoms or groups concerned, be any even number from 4 to 16, 8 and 12 being by far the most common; or (2) that a single electron or even 3 electrons, instead of the usual 2, may sometimes form a bond. Each of these possibilities has evidence in its favor, but as yet there is no way of knowing which, if either, is the correct explanation or whether both may be right.

The Werner Theory of Valence. In the compound $CuSO_4$ the copper was formerly considered to have a " valence " of +2 and the sulfate to have a " valence " of −2. On this basis alone, it is obviously impossible to explain the formation of the compound $Cu(NH_3)_4SO_4$ from a supposedly " neutral " molecule of $CuSO_4$ and supposedly neutral NH_3 molecules. Likewise, other complex compounds are formed with complete disregard for the traditional rules of valence. This difficulty was recognized many years ago but was completely unresolved until Werner, in 1891, long before the development of the electronic theory of valence, introduced a theory which systematized the study of such compounds and to a large extent explained their structure and behavior.

Werner postulated the existence of two types of valence: (1) primary valence, by means of which the copper and the sulfate, in the above example, are held together, and (2) secondary, auxiliary or coordinate valence, by means of which " neutral " molecules such as NH_3 may be joined to other neutral molecules without affecting the primary valences in the molecules so joined. It is the primary valence of Werner that has been traditionally known as the valence of an element or radical.

Werner assigned a definite secondary valence to an element or radical, the value depending upon the number of molecules, such as NH_3, which could combine with one atom of the element or a single one of the groups. Just as some elements may have a variable primary valence, so also they may have a variable secondary valence. The number of units of secondary valence is called the **coordination number** of the atom exhibiting the valence; thus, in $Cu(NH_3)_4SO_4$ the coordination number of copper is 4. The values of the coordination number range from 2 to 8, with 4 and 6 by far the most frequent in occurrence. The combination of the central atom and the groups attached to it by secondary valence bonds is called the coordinated group and is distinguished from the rest of the molecule by enclosing it in brackets, as in the formula $Cu(NH_3)_4SO_4$. Werner used a dotted line to indicate a secondary valence bond; this representation is still in common use.

The idea of secondary valence was very extensively developed by Werner and by others. It was discovered that the maximum value of the coordination number may be closely correlated with the position of the element in the periodic table, the maximum value increasing with increase in the atomic number of the element

This would seem to indicate a dependence of the coordination number on the size of the central atom, which would suggest some sort of regular geometrical arrangement of the coordinated molecules about the central atom. Considerable evidence indicates that this is a correct interpretation.

The Electronic Explanation of Werner's Theory. The student has undoubtedly noted by this time the similarity between Werner's primary valence and the polar valence of the electronic theory, as well as that between his secondary valence and what we have described previously as coordinate valence. This is more than an accidental resemblence; in fact, they are essentially the same theory expressed in different terms. The relationship may be made still more apparent by considering a few more aspects of Werner's theory.

An important feature of the theory is that it is possible for a singly charged anion to take the place of one of the neutral molecules in the coordinated group, but when this occurs the charge on the coordinated group is changed by an amount equal to the charge on the replacing ion. Any ion so included in the coordinated group loses many of its characteristic properties; chloride ion, for instance, is no longer precipitated when silver nitrate is added.

We may now see the application of the above features to some specific compounds. For this purpose we may use for the central atom trivalent cobalt which has a maximum coordination number of 6 and, as will be learned later, forms a great number of complex ions. The complex ion formed with ammonia should have the formula $[Co(NH_3)_6]^{+++}$, but this happens to be only one of a series of complex ions containing cobalt and ammonia. This series is of no particular importance in itself as far as we are concerned, but it illustrates so well the range of possibilities in the formation of such ions that we may be justified in examining it in some detail.

If we consider the $[Co(NH_3)_6]^{+++}$ ion and replace the ammonia molecules one by one by a singly charged anion, which we may designate by X, ions of the following compositions and charges will be obtained:

$$[Co(NH_3)_5X]^{++} \qquad [Co(NH_3)_4X_2]^{+} \qquad [Co(NH_3)_3X_3]^{0}$$
$$[Co(NH_3)_2X_4]^{-} \qquad [Co(NH_3)X_5]^{=} \qquad [CoX_6]^{\equiv}$$

Many compounds containing the above ions, X being Cl^-, NO_3^-, $\frac{1}{2}SO_4^{=}$ or some similar group, have been prepared. The changes

in color of cobalt solutions when ammonium hydroxide is added may be interpreted as being due to a change from one to another of the above ions.

The explanation of the formation of this series of compounds on the basis of the electronic theory is relatively simple. In the $[Co(NH_3)_6]^{+++}$ ion the cobalt ion has a coordination number of 6, i.e., 6 pairs of electrons have been shared with it, 1 pair coming from each of the 6 NH_3 molecules. If, by some means, one of these NH_3 molecules were to be removed from the coordinated group, taking with it both of the shared electrons, the cobalt ion would have an unsatisfied secondary valence, that is, an incomplete group of electrons, and would be in a position to form another coordinate bond with some other molecule or ion. The chloride ion, for example, having 4 pairs of electrons not shared with any atom, is able to supply the 2 electrons needed by the cobalt and accordingly enters the coordinated group. However, since the chloride ion carries one unit of negative charge, the net charge of the coordinated group is lowered by this amount, giving the formula $[Co(NH_3)_5Cl]^{++}$. Also, since the chloride ion is now attached by means of a coordinate bond it is no longer able to give the reactions characteristic of the simple ion; for instance, it is not precipitated as AgCl when $AgNO_3$ is added. By a repetition of the above process, until finally no more NH_3 molecules remain in the coordinated group, each of the other ions may be formed.

Throughout this discussion we have been speaking only of ions, but it has probably been noted that one member of the series is not an ion but a non-ionized compound. Compounds of this type, e.g., $[Co(NH_3)_3(NO_3)_3]$, are those in which there have been introduced just enough negatively charged ions to compensate for the positive charge of the original ion, leaving the entire coordinated group uncharged or non-ionized and hence analogous to non-ionized organic compounds such as chloroform. Such non-ionized organic compounds are usually insoluble in water but soluble in ether or alcohol, distillable and rather inert chemically; similarly, compounds of the above type, even though they may be purely inorganic, are analogous in many points of behavior to the non-ionized organic compounds.

So far we have considered only purely inorganic complex ions. There are, however, many organic molecules, such as urea, pyridine, ethylenediamine, hexamethylenetetramine and many others, which

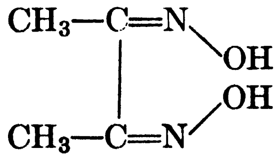
readily enter the coordinated group and give rise to the so-called metallo-organic compounds. Many of these organic compounds contain nitrogen and it can be shown that usually, if not invariably, there is an unshared pair of electrons on the nitrogen atom, by means of which a coordinate bond may be formed with the central atom. The compounds that do not contain nitrogen can also be shown to possess such an unshared electron pair at some point in the molecule. By making electronic diagrams, the student may prove to himself that the groups $-\overset{O}{\overset{\|}{C}}-$ and $=N-O-H$, for example, always contain such a pair on the oxygen and nitrogen atoms, respectively.

Such organic compounds as tartaric acid, citric acid and sugars interfere with the normal reactions of iron, cobalt and other metals. Examination of the formulas of these substances will show that each contains several $-\overset{O}{\overset{\|}{C}}-$ groups, indicating that it is possible for them to enter the coordinated group of the metal, forming complex ions and thus, as would be expected, giving a behavior different from that usually attributed to the metallic ion itself. The formation of such complex ions may, if they are distinctively colored, serve as a qualitative test for the metal ion. Examples of this sort are found in the descriptions of the reactions of the metals.

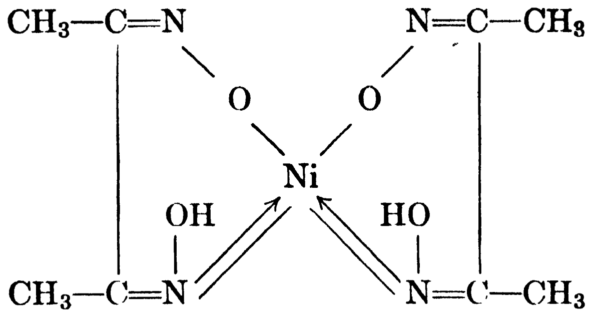
Chelate Compounds. Thus far in the discussion of complex ions and compounds we have mentioned only those in which a molecule in the coordinated group has only one point of attachment to the central atom. It is perfectly possible, however, for the same molecule to be attached to the central atom at two points, thus forming a ring structure. Compounds having such a structure have been called inner-complex compounds or chelate compounds, the work chelate, meaning "clawlike," suggesting the manner in which the molecule is attached to the central atom.

The molecule may be attached to the central atom by 2 covalent bonds, by 1 covalent and 1 coordinate bond or by 2 coordinate bonds. Of these three possibilities only the latter two will be considered here; we shall make no effort to distinguish between them, although it is possible to do so. The nature of these chelate compounds is best explained by consideration of a specific example.

Nickel, which commonly has a primary valence of 2 and a coordination number of 4, forms with dimethylglyoxime (see page 174).



a compound having the structure:



It will be noticed that each of the two organic molecules is attached to the nickel at two points, forming 2 six-membered rings — a chelate compound. It is seen that nickel has taken the place of a hydrogen atom in each of the two organic molecules, forming covalent bonds with the oxygen atoms to which the hydrogen was originally attached. The originally unshared pair of electrons on the nitrogen atoms of the other two = N — OH groups now form 2 coordinate bonds with the nickel.

Dyeing with the use of a mordant, and analytical tests depending upon such a process, may also be explained as being due to the formation of chelate compounds. The aluminon test for aluminum illustrates this. When aluminon, a red dyestuff, is added to an acid solution containing aluminum, the red color is distributed uniformly throughout the solution. The addition of ammonium hydroxide to this solution results in the formation of clumps of hydrated aluminum oxide which are colored bright red by the dye. The dye collects on the precipitate, leaving the solution practically colorless. Dyes which behave in this way have groups that favor the formation of chelate compounds, and although frequently the actual structure of the colored material is totally unknown, it is highly probable that it is a chelate compound.

A material like hydrated aluminum oxide which combines with a dye and forms a stable colored complex is called a **mordant**; the

combination of a mordant and a dye is called a **lake.** Lakes are frequently described as being adsorption complexes, but it is probable that, in this case at least, "adsorption" is to be interpreted as an actual chemical combination.

By far the greater number of chelate compounds have rings containing 5 or 6 atoms. A ring of this size seems to give greater stability than one containing fewer than 5 or more than 6 atoms. Students of organic chemistry will recognize this fact as further evidence in support of the Baeyer strain theory of ring formation.

Although the chelate compounds that are of the greatest importance in analytical chemistry are those that are insoluble in water, it must not be supposed that all of them are insoluble. On the contrary, such soluble materials as the complex compounds formed by iron and cobalt with tartrates and citrates are probably chelate compounds.

REVIEW EXERCISES — SET 6

1. What is the Werner theory of valence? Show how it applies to some specific complex compounds.

2. Explain Werner's theory in terms of electrons. Account for the formation of series of complex ions by replacement of groups within the coordinated group.

3. What are chelate compounds? Illustrate.

4. List the complex ammonia ions that are encountered in the scheme of cation analysis.

5. Find in the cation scheme examples of separations that depend upon the relative stabilities of 2 or more complex ions.

6. Mention some precipitates, formed in the cation analysis, which are dissolved with the formation of complex ions.

7. What are hydrates? Hydrated oxides? Describe their structure on the basis of complex-ion formation.

8. Why do tartrates, citrates and similar organic anions interfere with the cation analysis? Why do they interfere more seriously with such metals as iron and copper than with metals like calcium or sodium?

9. What is the concentration of Cu^+ in a solution that is 0.001 M in CN^- and contains 0.1 gram-ion per liter of $Cu(CN)_4^{=}$?

10. What concentration of NH_3 must be present to keep C_{Ag^+} down to 0.0_41 gram-ion per liter in a solution containing 1 gram-ion per liter of $Ag(NH_3)_2^+$?

11. From the instability constant of $Cu(NH_3)_4^{++}$ and the $K_{s.p.}$ of CuS, calculate whether CuS would be expected to dissolve in a 10.0 M solution of NH_3. Hint: Find whether CuS or the complex ion gives the larger Cu^{++} concentration.

12. Which would contain the larger concentration of Ag^+: a solution 0.1 M in $Ag(NH_3)_2^+$ and 0.1 M in NH_3 or a solution 1.0 M in $Ag(CN)_2^-$ and 0.01 M in CN^-?

AMPHOTERISM

An amphoteric or amphiprotic compound is one which has the properties of both an acid and a base. Many oxides and hydroxides are amphoteric and ionize as acids and as bases. This is especially true of the hydroxides of the elements occupying positions near the middle of the periodic table (see page 115). Of special interest to us are the hydroxides of aluminum, chromium, zinc, antimony and tin.

Aluminum hydroxide will be taken here as a typical example to illustrate the behavior of amphoteric hydroxides. The ionization of $Al(OH)_3$ as a base can be represented thus:

$$Al(OH)_3 \rightleftharpoons Al^{+++} + 3OH^-$$

and as an acid:

$$(HO)_3Al \rightleftharpoons H^+ + AlO_2^- + H_2O$$

yielding H^+ ion from its primary ionization, the meta-aluminate ion, AlO_2^-, and H_2O. In an aqueous solution of aluminum hydroxide [a very dilute one, since $Al(OH)_3$ is very sparingly soluble in water] there exist aluminum and hydroxyl ions in equilibrium with hydrogen and meta-aluminate ions. On the basis of this double equilibrium we can see why, on the one hand, $Al(OH)_3$ will dissolve in acids to form aluminum salts and, on the other hand, why it will dissolve in bases to form aluminates. In the first case, the hydroxyl ions coming from the ionization of $Al(OH)_3$ are used up by the hydrogen ions from the acid, and this results in more solid being dissolved to restore equilibrium; the comparatively high hydrogen-ion concentration forces back the ionization of $Al(OH)_3$ as an acid. In the second case when an alkali such as NaOH is added to $Al(OH)_3$ the hydrogen-ion concentration is lowered by neutralization and at the same time the ionization of $Al(OH)_3$ as a base is repressed; to again restore equilibrium, more solid must dissolve and ionize. Thus in both cases final equilibrium is established when all the solid has dissolved.

The tendency for $Al(OH)_3$ to ionize as a base is somewhat more marked than its tendency to ionize as an acid; in other words, a saturated solution of aluminum hydroxide contains slightly more hydroxyl ions than hydrogen ions. With $Zn(OH)_2$ the basic tendency is still more marked; with certain other amphoteric hydroxides the acid tendency predominates.

The Electronic Explanation of Amphoterism. A hydroxide, *M*OH, where *M* may be a single element or a radical, has two possible modes of ionization: it may form M^+ and OH^- or H^+ and MO^- ions. The form that predominates is determined by the tendency of *M* to attract or give up electrons. This can be made clear in the following way:

The molecule *M*OH is held together by 2 electron-pair bonds. Suppose first of all that *M* is H or some group which has the same attraction for electrons as H. The 2 pairs of electrons will then be shared approximately equally; that is, they will be the same distance, call it *a*, from the O atom:

$$M^{+}\overset{a}{\overbrace{{}^{\circ}_{\circ}\ \mathrm{O}\ {}^{\circ}_{\circ}}}\overset{a}{}\mathrm{H}^{-}$$

Next, if *M* is some group which has a very slight attraction for electrons, the electron pair on the left will be displaced toward the oxygen and if the displacement is sufficient an ionic bond is formed between *M* and O, that is, the compound consists of the ion M^+ and OH^-. It may be noted ther that, since the O atom has but a limited ability to attract and hold electrons, if the pair on the left is moved closer to the O the pair on the right must move farther away, i.e., closer to the H. This latter effect corresponds to a decrease in the tendency to liberate a hydrogen ion, which may be one reason why we do not observe ionization into M^+, H^+, and $O^=$ ions. The following diagram illustrates the situation:

$$M^{+}\ \overset{a\ a}{\overbrace{{}^{\circ}_{\circ}\ \mathrm{O}\ {}^{\circ}_{\circ}}}\ \mathrm{H}^{-}$$

The remaining possibility is that *M* may be some group which has a very strong attraction for electrons. In this case the electron pair on the left will be displaced toward *M* and that on the

right toward O or away from H:

$$ {}^{-}M \underbrace{\overset{\circ}{\underset{\circ}{}}\ \mathrm{O}\ \overset{\circ}{\underset{\circ}{}}}^{a\ a} \mathrm{H}^{+} $$

If this effect is sufficiently pronounced it means that the compound is ionized into H^+ and MO^- ions.

Since the OH^- ion is a base we may refer to ionization according to the first scheme as ionization as a base and according to the second scheme as ionization as an acid.

The elements in Groups I and II of the periodic table (see page 115) have a pronounced tendency to give up electrons and therefore their hydroxides are ionized as bases; these elements form the strong alkali hydroxides, such as NaOH and KOH. Similarly, the elements of Groups VI and VII of the periodic table have a considerable tendency to attract electrons. Therefore, if M is a radical containing an element of these groups the hydroxide will be ionized as an acid; these elements from the strong oxygen acids, such as $SO_2(OH)_2$ or H_2SO_4 and ClO_3OH or $HClO_4$.

But what of the elements of Groups III, IV and V? Most of these elements have no decided tendency either to repel or to attract electrons and therefore rarely, if ever, form simple ions. The hydroxides of most of these elements, as would be expected, show no decided tendency to ionize either as acids or as bases and, in fact, show both kinds of ionization simultaneously. If such hydroxides are in an acid environment the OH^- will be removed by combination with H^+ and the ionization as a base will be favored; similarly, in an alkaline environment the ionization as an acid is favored:

$$MO^- + H^+ \rightleftharpoons MOH \rightleftharpoons M^+ + OH^-$$

$$MOH + H^+ \rightleftharpoons M^+ + H_2O \quad \text{(acid environment)}$$

$$MO^- + H_2O \rightleftharpoons OH^- + MOH \quad \text{(alkaline environment)}$$

Amphoterism is shown especially by the hydroxides of the elements of Groups III, IV and V of the periodic table; the hydroxides of N and P, however, are decidedly more acidic than basic in character. The most decidedly amphoteric elements are found near a line drawn diagonally from the upper left- to the lower right-hand corner of the periodic table in its usual form; elements such as N and P which are not relatively near this line are not

likely to be appreciably amphoteric even though they may be in Group III, IV and V.

As we go from top to bottom in a main group of the periodic table the size of the atoms increases and so the ability of the nucleus to hold electrons in the outermost orbit decreases; the ability to attract extra electrons to this orbit also decreases. This means that for any main group the basicity of the hydroxides will increase or — to say the same thing in another way — the acidity of the hydroxides will decrease in going from top to bottom in the table. Hence, considering the groups at the left in the table, the tendency to be amphoteric will be greatest for the elements at the top for the groups at the right the tendency will be greatest for the elements at the bottom.

It must not be supposed that the hydroxides are the only compounds that exhibit amphoterism. As is to be expected from the analogous behavior of sulfur and oxygen compounds, the sulfides of many metals are also amphoteric. We can illustrate the similarity in the following way:

Antimony oxide is a typical amphoteric compound. This oxide is soluble in either strongly acid or alkaline solutions:

$$Sb_2O_3 + 6H^+ + 8Cl^- \rightarrow 2SbCl_4^- + 3H_2O$$

$$Sb_2O_3 + 2OH^- \rightarrow 2SbO_2^- + H_2O$$

The sulfide is likewise soluble in either acid or alkaline soultion:

$$Sb_2S_3 + 6H^+ + 8Cl^- \rightarrow 2SbCl_4^- + 3H_2S$$

$$2Sb_2S_3 + 4OH^- \rightarrow 3SbS_2^- + SbO_2^- + 2H_2O$$

If instead of an alkali hydroxide an alkali sulfide, such as Na_2S, is used, solution of Sb_2S_3 takes place in much the same way:

$$S^= + H_3O^+ \rightarrow SH^- + H_2O$$

$$Sb_2S_3 + 2SH^- \rightarrow 2SbS_2^- + H_2S$$

The amphoteric nature of hydroxides and sulfides is utilized in qualitative analysis to effect a number of separations. Of particular importance is the separation of the Group II sulfides into two divisions and the separation of aluminum, chromium and zinc from iron and manganese in Group III. The student should refer to these sections of the systematic scheme and write the equations involved by analogy with those given for Sb_2S_3 and $Al(OH)_3$.

others taking place in aqueous solutions, reach an equilibrium. How the equilibrium constants for such reactions are calculated and how relative oxidizing and reducing ability are measured will now be shown.

The dissolving of a metal, i.e., passing from the solid (atomic) state to the ionic condition, is a simple case of oxidation, as for instance, in the case of zinc:

$$Zn^0 \rightarrow Zn^{++} + 2e$$

the action being accompanied by the loss of 2 electrons for each ion formed. Conversely, when the ion of a metal gains electrons and is deposited in the metallic condition, the process is one of reduction, as in the case of the deposition of copper:

$$Cu^{++} + 2e \rightarrow Cu^0$$

The formation of zinc ions, when a strip of zinc is placed in water or in a dilute solution of a zinc salt, will leave the strip negatively charged and the solution positively charged. There is thus set up a difference of electrical potential at the contact of the metal and its solution. The value of the potential difference depends, among other factors, on the " solution pressure " of the metal to tend to drive atoms into solution and on the osmotic pressure to act in the opposite direction to force ions out of solution. Nernst has derived the following equation for this potential difference, E:

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

in which C, the concentration of ions in the solution, is substituted for the osmotic pressure; k is the so-called Nernst constant, substituted for the solution pressure; n is the valence change, and 0.059 a constant (here given for 25° C.).

There is no direct way by which the value of E can be determined but relative values can be obtained by making the strip of metal with its solution one of the electrodes of a voltaic cell, the other electrode being either a standard hydrogen or a standard calomel electrode.

A standard or " normal " hydrogen electrode consists of a small strip of platinum coated with platinum black and joined to a wire encased in a glass tube. The tube is surrounded by another larger tube through which a stream of hydrogen is passed. This arrange-

TABLE VIII

Potential Series

Equation for Half-Cell Reaction			Half-Cell Potential in Volts
K	$\rightleftharpoons K^+$	$+ 1e$	-2.922
Ba	$\rightleftharpoons Ba^{++}$	$+ 2e$	-2.90
Ca	$\rightleftharpoons Ca^{++}$	$+ 2e$	-2.87
Na	$\rightleftharpoons Na^+$	$+ 1e$	-2.712
Sr	$\rightleftharpoons Sr^{++}$	$+ 2e$	-2.89
Mg	$\rightleftharpoons Mg^{++}$	$+ 2e$	-2.34
Al	$\rightleftharpoons Al^{+++}$	$+ 3e$	-1.67
Mn	$\rightleftharpoons Mn^{++}$	$+ 2e$	-1.05
Zn	$\rightleftharpoons Zn^{++}$	$+ 2e$	-0.7620
Cr	$\rightleftharpoons Cr^{+++}$	$+ 3e$	-0.71
$S^=$ (basic)	$\rightleftharpoons S$	$+ 2e$	-0.508
Fe	$\rightleftharpoons Fe^{++}$	$+ 2e$	-0.440
Cd	$\rightleftharpoons Cd^{++}$	$+ 2e$	-0.4020
Co	$\rightleftharpoons Co^{++}$	$+ 2e$	-0.277
Ni	$\rightleftharpoons Ni^{++}$	$+ 2e$	-0.250
Sn	$\rightleftharpoons Sn^{++}$	$+ 2e$	-0.136
Pb	$\rightleftharpoons Pb^{++}$	$+ 2e$	-0.126
Fe	$\rightleftharpoons Fe^{+++}$	$+ 3e$	-0.036
H_2	$\rightleftharpoons 2H^+$	$+ 2e$	0.00
$S^=$ (acid)	$\rightleftharpoons S$	$+ 2e$	$+0.141$
Sn^{++}	$\rightleftharpoons Sn^{++++}$	$+ 2e$	$+0.15$
Cu^+	$\rightleftharpoons Cu^{++}$	$+ 1e$	$+0.167$
$H_2O + Sb$	$\rightleftharpoons SbO^+ + 2H^+$	$+ 3e$	$+0.212$
$2H_2O + As$	$\rightleftharpoons HAsO_2(aq.) + 3H^+$	$+ 3e$	$+0.2475$
$H_2O + Bi$	$\rightleftharpoons BiO^+ + 2H^+$	$+ 3e$	$+0.32$
Cu	$\rightleftharpoons Cu^{++}$	$+ 2e$	$+0.3448$
$Fe(CN)_6^{-4}$	$\rightleftharpoons Fe(CN)_4^{-3}$	$+ 1e$	$+0.36$
$4OH^-$	$\rightleftharpoons O_2 + 2H_2O$	$+ 4e$	$+0.401$
Cu	$\rightleftharpoons Cu^+$	$+ 1e$	$+0.522$
$2I^-$	$\rightleftharpoons I_2$	$+ 2e$	$+0.5345$
$HAsO_2 + 2H_2O$	$\rightleftharpoons H_3AsO_4 + 2H^+$	$+ 2e$	$+0.559$
$MnO_2 + 4OH^-$	$\rightleftharpoons MnO_4^- + 2H_2O$	$+ 3e$	$+0.58$
Fe^{++}	$\rightleftharpoons Fe^{+++}$	$+ 1e$	$+0.771$
$2Hg$	$\rightleftharpoons Hg_2^{++}$	$+ 2e$	$+0.7986$
Ag	$\rightleftharpoons Ag^+$	$+ 1e$	$+0.7995$
Hg	$\rightleftharpoons Hg^{++}$	$+ 2e$	$+0.854$
Hg_2^{++}	$\rightleftharpoons 2Hg^{++}$	$+ 2e$	$+0.910$
$NO + 2H_2O$	$\rightleftharpoons NO_3^- + 4H^+$	$+ 3e$	$+0.96$
$2Br^-$	$\rightleftharpoons Br_2$	$+ 2e$	$+1.0652$
Au^+	$\rightleftharpoons Au^{+++}$	$+ 2e$	$+1.3$
$2Cl^-$	$\rightleftharpoons Cl_2$	$+ 2e$	$+1.3583$
$2Cr^{+++} + 7H_2O$	$\rightleftharpoons Cr_2O_7^= + 14H^+$	$+ 6e$	$+1.36$
Au	$\rightleftharpoons Au^{+++}$	$+ 3e$	$+1.42$
$Mn^{++} + 4H_2O$	$\rightleftharpoons MnO_4^- + 8H^+$	$+ 5e$	$+1.52$

ment is placed in a vessel containing acid whose concentration of H^+ ions is exactly 1. Such an electrode is arbitrarily assigned a potential of zero.

If then a zinc electrode is joined, by an external circuit through a voltmeter or potentiometer, to a hydrogen electrode and the two solutions are connected by means of a tube containing a conducting salt solution, the voltage indicated on the instrument will be the difference between that of the zinc electrode and that of the hydrogen electrode. Since the standard hydrogen electrode potential has been taken as 0, that of the zinc electrode will be the value indicated. In this way it has been found that for a zinc electrode, when the concentration of zinc ions is exactly molar, the potential is -0.76 volt. Similarly, for a copper electrode, the molar potential is $+0.34$ volt. Values for practically all the metallic elements have in this way been determined. When arranged in order, they constitute the familiar potential series or electromotive series of metals. The more common metals are incorporated in Table VIII.

The electrode potential is a measure of the ease with which the metal is converted from the atomic to the ionic state. The higher the position of the metal in the series, the more readily it becomes oxidized; the reducing action of the metal decreases as we go down through the series. Since, for example, from the relative positions of zinc and copper in the series, zinc is more easily oxidized than copper, a piece of metallic zinc placed in a solution of a cupric salt will reduce the Cu^{++} ions to metallic copper, the zinc going into solution as Zn^{++} ions and depositing the copper. For the same reason aluminum will deposit antimony, and iron will reduce stannic ions. There are many important applications of this kind in analytical chemistry.

Calculation of Equilibrium Constant. In the replacement of copper by zinc, the reaction is:

$$Zn^0 + Cu^{++} \rightleftharpoons Zn^{++} + Cu^0$$

Applying the Law of Chemical Equilibrium to this reaction, the equilibrium equation becomes:

$$\frac{C_{Zn^{++}} \times C_{Cu^0}}{C_{Cu^{++}} \times C_{Zn^0}} = K$$

and equilibrium is reached when the value of K is satisfied. Since

the factors C_{Cu^0} and C_{Zn^0} represent the solid, metallic condition, they may be considered constant quantities and the above equation becomes simply:

$$\frac{C_{Zn^{++}}}{C_{Cu^{++}}} = K \quad \text{(equilibrium constant)}$$

This means that when the concentration of zinc ions bears a certain ratio to that of the copper ions, the reaction will have reached equilibrium. The equilibrium ratio, i.e., the equilibrium constant K, for this reaction is calculated from electrochemical considerations, using electrode potentials and applying the Nernst equation.

If the strip of zinc is immersed in a solution of a zinc salt and is made one electrode of a voltaic cell, and a strip of copper dipping into a copper salt solution is made the other electrode, and if the two electrodes are joined externally through a voltmeter and internally by a conducting salt solution, as a result of the passage of electrons from the zinc electrode, electric current will flow through the instrument to the copper electrode. The current will cease when the system has come to equilibrium; this will occur when the electrode potential of the zinc equals that of the copper.

The Nernst equation:

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

may be expanded into the form:

$$E = \frac{0.059}{n} \log \frac{1}{k} + \frac{0.059}{n} \log C$$

When the concentration is molar, $C = 1$, and the molar potential E_0 is given by $(0.059/n \log 1/k)$. From this the potential of the electrode for any concentration may be expressed by the equation:

$$E = E_0 + \frac{0.059}{n} \log C$$

In the case of the zinc electrode:

$$E_{(\text{zinc})} = E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{Zn^{++}}$$

and for the copper electrode:

$$E_{(\text{copper})} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{Cu^{++}}$$

At equilibrium, when $E_{(zinc)}$ is equal to $E_{(copper)}$,

$$E_{0(zinc)} + \frac{0.059}{2} \log C_{Zn^{++}} = E_{0(copper)} + \frac{0.059}{2} \log C_{Cu^{++}}$$

From Table VIII:

$$-0.76 + 0.0295 \log C_{Zn^{++}} = 0.34 + 0.0295 \log C_{Cu^{++}}$$
$$1.10 = 0.0295 (\log C_{Zn^{++}} - \log C_{Cu^{++}})$$
$$\log \frac{C_{Zn^{++}}}{C_{Cu^{++}}} = 37.3$$
$$\frac{C_{Zn^{++}}}{C_{Cu^{++}}} = 1 \times 10^{37.3} \text{ or } 2 \times 10^{37}$$
$$\therefore K = 2 \times 10^{37}$$

Therefore, K, the ratio of the Zn^{++} ion concentration to that of the Cu^{++} ion concentration is 2×10^{37}. This means that when equilibrium is reached in the reaction in which zinc ions displace copper ions, the concentration of Zn^{++} is enormous, and the concentration of Cu^{++} remaining in solution is negligible; for practical purposes the removal of cupric ions is complete.

When a non-metallic element, such as sulfur or chlorine, dissolves, negatively charged ions (anions) are formed, and the process is one of reduction. In the case of chlorine, for example, the reaction is:

$$Cl_2^0 + 2e \rightleftharpoons 2Cl^-$$

The Nernst equation for non-metallic electrodes takes the form:

$$E = -\frac{0.059}{n} \log \frac{C_{anion}}{k}$$

Since, however, C_{anion}, the concentration of the ion, is dependent upon the solubility of the gas, the equation is transformed into

$$E = \frac{0.059}{n} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2 \times k}$$

and the molar electrode potential is given by:

$$E_{(Cl)} = E_{0(Cl)} + \frac{0.059}{2} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2}$$

E_0 for chlorine has been found to be +1.3583 volts. The corresponding value of E_0 for iodine is +0.5345 volt. (See Table VIII) The values show chlorine to be a stronger oxidizing agent than iodine and the iodide ion a stronger reducing agent than the chloride ion. Chlorine therefore will oxidize iodides, in accordance with the equation:

$$Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2$$

The equilibrium constant of this reaction is expressed by the equation:

$$\frac{(C_{Cl^-})^2 \times C_{I_2}}{(C_{I^-})^2 \times C_{Cl_2}} = K$$

Applying the same electrochemical method as used in determining the Zn^{++}/Cu^{++} ratio, when equilibrium is reached, a cell consisting of a chlorine electrode joined with an iodine electrode will show equilibrium when the potentials of the two electrodes are equal. We have then:

$$E_{0(Cl)} + \frac{0.059}{2} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2} = E_{0(I)} + \frac{0.059}{2} \log \frac{C_{I_2}}{(C_{I^-})^2}$$

$$\frac{0.059}{2}\left(\log \frac{C_{I_2}}{(C_{I^-})^2} - \log \frac{C_{Cl_2}}{(C_{Cl^-})^2}\right) = 1.3583 - 0.5345$$

$$\log \frac{(C_{Cl^-})^2 C_{I_2}}{(C_{I^-})^2 C_{Cl_2}} = 27.90$$

$$\log K = 27.90$$

$$K = 1 \times 10^{27.90} \text{ or } 7.9 \times 10^{27}$$

The value of K shows that the reaction runs very far to completion.

Equilibrium in other Oxidizing-Reducing Systems. With elements which exist in two different ionic forms such as, for example, the reversible change for the oxidation of ferrous ions and reduction of ferric ions:

$$Fe^{++} \rightleftharpoons Fe^{+++} + 1e$$

and with the more complex relationships, as in the oxidation of manganous ion and reduction of the MnO_4^- ion in an acidic solution:

$$Mn^{++} \rightleftharpoons MnO_4^- + 8H^+ + 5e$$

the molar potentials can be determined and the ions arranged into

similar series. The more important ones for which data exist are given in Table VIII.

Equilibrium constants for any interaction between an oxidizing substance and a reducing substance can be calculated from electrochemical data. For the reaction:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

rewritten in ionic form:

$$5Fe^{++} + MnO_4^{-} + 8H^{+} \rightleftharpoons 5Fe^{+++} + Mn^{++} + 4H_2O$$

the equilibrium constant is expressed by

$$\frac{(C_{Fe^{+++}})^5 \times C_{Mn^{++}}}{(C_{Fe^{++}})^5 \times C_{MnO_4^-} \times (C_{H^+})^8} = K$$

By combining the potentials for the $Fe^{++} - Fe^{+++}$ and $Mn^{++} - MnO_4^{-}$ half-cells the value of the constant can be found. In this way one can calculate whether any particular oxidation-reduction reaction will take place and, if it does, how near to completion it will go before equilibrium is attained.

REVIEW EXERCISES — SET 9

1. What is a half-cell? A salt bridge? A standard hydrogen electrode?

2. Calculate the equilibrium constant for the displacement of Ag by Pb.

3. Will metallic iron reduce stannic ions to the stannous condition? Answer by reference to Table VIII.

4. Magnesium is above aluminum in the table. Why does aluminum not plate out when a strip of magnesium is placed in a solution of an aluminum compound?

5. What potential would be developed at 25° by a cell consisting of a molal Mg half-cell and a molal Pb half-cell?

6. Apply Nernst's equation to two half-cells made up of the same electrode material and containing the same electrolyte, but at two different concentrations. Combine the two equations and thus obtain the expression for the potential of a concentration cell.

7. Apply the result of question 6 to two $Zn - ZnSO_4$ half-cells, one containing 1 molal $ZnSO_4$ and the other 0.1 molal $ZnSO_4$. What is the potential of the combination? What is the electrode reaction in each half-cell? When will equilibrium be attained?

8. If you wish to prepare Cl_2 by oxidizing HCl, is $KMnO_4$ or $K_2Cr_2O_7$ the better oxidizing agent? Answer by reference to Table VIII.

9. Why is Cl_2 liberated instead of O_2 when a solution of NaCl is electrolyzed?

10. Suppose that you had a solution containing Au^{+++}, Ag^{+}, Cu^{++}, and Cd^{++}. How would you proceed to separate them electrolytically?

11. Find the equilibrium constant for the reaction between I^{-} and Br_2.

12. If you wished to use H_2S as a reducing agent would it be more effective to have the solution acid or basic?

PART II

THE REACTIONS OF THE CATIONS

GENERAL INSTRUCTIONS CONCERNING LABORATORY WORK

Upon being assigned a locker, check over the equipment contained therein and examine each piece carefully for imperfections, such as scratches, cracks, excessive etching and especially note any missing items from the lists of permanent and non-returnable apparatus supplied.

Procure a supply of concentrated HCl, HNO_3, H_2SO_4 and ammonia, for individual use, and place these reagents in labeled 250-ml. bottles, unless some other provision has been made for dispensing them.

Cleaning Solution. It is important that all apparatus be clean at all times. Soap solution or sodium phosphate is usually used for this purpose. Dichromate cleaning solution is sometimes recommended in place of the other two. In order that this cleanser be sufficiently cool before the close of the laboratory period, it is imperative that its preparation be attended to without further delay.

The dichromate cleaner is made as follows: Dissolve 50 grams of commercial $Na_2Cr_2O_7$ in 150 ml. of warm water. Cool and add slowly, with constant stirring, 230 ml. of commercial H_2SO_4. The mixing is best done in a large evaporating dish. When thoroughly cool, at the close of the laboratory period, transfer to a 500-ml. wide-mouthed bottle and use as required. This cleaning mixture can be used repeatedly as long as it remains red and thick.

To use this cleaning agent, pour enough into the apparatus to coat the inside walls with the red precipitate, returning the excess to the bottle, and allow the vessel to stand for some time. Rinse first with tap water, then with a small quantity of distilled water; place upside down and allow to drain onto a clean towel spread on the desk or in the locker.

Always rinse apparatus with distilled water immediately before use. *Use distilled water sparingly.*

Wash Bottle. A wash bottle should next be made. This is made from a 500-ml. Florence flask according to the directions given by the instructor. The nozzle should be attached to the outlet tube by a piece of rubber tubing so that it can be manipulated by the hand and the stream of water directed in the desired direction.

Two stirring rods are to be made, from glass rods 6 inches long, by fire-polishing both ends.

A platinum wire is to be sealed into a 6-inch length of glass tubing.

Preparation of Locker Reagents. Dilute solutions of HCl, H_2SO_4, HNO_3 and ammonia are to be prepared by the student and kept in his locker. These reagents are made by diluting the "concentrated" reagents with distilled water. The correct amount of water must be computed from the specific gravity and the percentage by weight of the original and final solution according to the method given in Part I, page 23, where examples of dilution calculations are given.

GENERAL RULES OF LABORATORY TECHNIQUE

Some general rules in regard to the operations involved in the experimental or laboratory work of this course can be stated at the outset. These rules must be adhered to and diligently followed if correct technique is to be acquired and the results, especially of the analysis of samples, are to be successful.

Cleanliness. Do not allow pools of water to collect on the desk top; use a sponge and towel freely. Never allow filtrate from a funnel to drop onto the base of the filter stand; provide a receptacle to catch the filtrate. If an accident occurs which results in broken apparatus and spilled solutions, clean up the wreckage and cheerfully begin the analysis over again.

Never put apparatus away in a dirty condition. Solutions set aside for subsequent analysis should always be placed in stoppered, properly labeled flasks. Have a definite place in the locker for each piece of apparatus; keep the ironware separate from the glassware. Sponge off the desk before leaving the laboratory.

Reagents. The reagents and test solutions required are made according to directions given in the Appendix (pages 323–325). They should not be carried from the reagent shelves; transfer the amount needed to a beaker or test tube. Do not allow the reagents to become contaminated; if by mistake they become so, discard the entire contents of the bottle, so that the work of others in the laboratory will not be rendered worthless by use of impure reagents. This rule applies to the solid reagents as well as the liquids. Never use more reagent than necessary to produce the desired result; too much is often worse than not enough. When freshly prepared reagents are called for make only sufficient for the immediate needs.

Precipitation. Most of the separations required in the course of an analysis are made by first forming a precipitate through the action of a reagent. The proper technique here is to add the reagent slowly, stirring constantly, until it is judged that precipitation is nearly complete and then to add more reagent dropwise. Complete precipitation can be ascertained by allowing the precipitate to settle and then adding a few drops of reagent to the supernatant liquid; or if the precipitate remains suspended, pour some of the solution through a filter and test the filtrate with the reagent. Continue addition of reagent to the main solution until tests show that precipitation is complete. A slight excess of precipitating agent should be used unless otherwise directed but too large an excess is harmful.

Precipitations are best made in hot solutions. In some cases it is necessary to allow the precipitate to remain in contact with the hot solution in order to bring about complete reaction or to produce larger particles of the precipitate. This process is called called **digestion.**

Residues are the solid portions remaining after the action of a dissolving or extracting agent; **precipitates** are the solids formed by ionic reactions.

Colloidal Precipitates. Certain types of precipitates have the tendency to remain finely divided. The particles are of colloidal size and give much trouble by remaining suspended and by passing through the pores of ordinary filters. This trouble can be avoided to a certain extent by adding electrolytes which will coagulate the colloidal particles into larger aggregates. Ammonium salts, such as NH_4NO_3, are frequently added to overcome colloid formation.

In some cases digestion is helpful in overcoming this difficulty. Colloidal precipitates and sols have been discussed on page 74.

Filtration. Precipitates and residues must be completely freed from their solutions by filtering and washing. A good quality of filter paper should be used. The paper should be folded twice, fitted snugly in the cone of the glass funnel and a small volume of water poured through. If the water does not filter rapidly and uniformly, use a new paper. In filtering a solution touch the stem of the funnel against the side of the receiving vessel; this will give more rapid filtration. Pour the liquid down a stirring rod placed against the lip of the beaker to prevent spattering. Pour off as much of the liquid as possible, add a little wash water to the solid, decant again and finally transfer the entire solid to the filter by partly inverting the beaker and directing a stream of water from a wash bottle onto the solid, thereby flushing it down the stirring rod and into the filter.

Washing. If the precipitate is of such a nature that it settles rapidly, several repeated additions of wash water can be made before the solid is finally transferred to the filter. This method is known as **washing by decantation** and should be used whenever possible. In other cases all the washing must be done on the filter. The best technique is to use several small portions of wash water, allowing the funnel to drain completely after each addition. Never use more wash liquid than necessary, because all precipitates are soluble to some extent and, moreover, if the volume of filtrate becomes too large, the excess must later be removed by evaporation. Always test for complete extraction. To do this, filter into a test tube a few milliliters of the liquid draining from the funnel when washing is thought complete and apply the proper reagent which will give a test for the substance being extracted from the residue. If the test is negative, extraction is complete.

When the filtrate comes through turbid, indicating a colloidal solution, the difficulty can usually be overcome by resorting to one of the following devices: (1) refiltering; (2) use of a double filter paper; (3) use of a filter paper of finer porosity; (4) digestion; (5) addition of NH_4NO_3 or other electrolyte to the wash water.

To lessen the solubility of a precipitate in pure water, a small quantity of the precipitating reagent is sometimes added to the wash water. This is another application of the common-ion principle.

Evaporation of Liquids. When it becomes necessary to reduce the volume of a solution, or to take it down to dryness, this is best done by heating in an evaporating dish or casserole over the water bath. The hot plate or free flame may be used, but care must be taken to prevent spattering and loss of solid residue during the expulsion of the last of the water.

It frequently becomes necessary to remove excess of strong acids from solutions or to replace one acid by another. The first result can be accompanied either by neutralization with a base or by evaporation. If the addition of the base to the solution is objectionable the acid must be removed by evaporating to dryness. Thus, for example, if it is desired to remove excess of hydrochloric acid from a solution, the solution is heated and steam and HCl are evolved in such proportions as to leave a 20.2 per cent solution of hydrochloric acid which has a constant boiling point of 110° C. This mixture upon further heating will not change its composition but can be evaporated and completely expelled at this temperature. The behavior of nitric acid is similar, the constant boiling mixture having a composition of about 68 per cent HNO_3 and boiling at 120° C. Sulfuric acid boils at a much higher temperature, the constant boiling mixture being reached at about 300° C. and consisting of about 98 per cent H_2SO_4. Phosphoric acid is even less volatile than sulfuric acid. The removal of HCl, HNO_3 and H_2SO_4 can therefore be effected by evaporating the constant boiling mixture to dryness, taking care, however, to prevent loss of residue by spattering.

To replace hydrochloric acid by nitric acid, that is, to change a solution containing chloride ions to one containing nitrate ions, add nitric acid and evaporate. The nitric acid decomposes the hydrochloric acid according to the reaction:

$$HNO_3 + 3HCl = Cl_2 + NOCl + 2H_2O$$

By repeating the addition of nitric acid and evaporating nearly to dryness, all of the hydrochloric acid will be decomposed and will leave the desired nitrate ions in solution. In a similar way, the change from nitrate to chloride is effected by adding hydrochloric acid in excess and evaporating one or more times.

To replace both nitric and hydrochloric acid by sulfuric acid, add concentrated H_2SO_4 and heat until dense white fumes of SO_3

are evolved; this will not occur until all of the hydrochloric and nitric acid is volatilized. This is known as **fuming down.**

Notebook.* A notebook of convenient size, in which all laboratory records are to be kept, should be provided. The record should include: (1) the results of the preliminary experiments, including the writing of equations for the reactions studied, the character of the precipitates or other products obtained and other notes bearing on the experiment being performed; (2) notes kept during the analysis of samples, covering the effect of reagents used, the results of each step involved, etc. In all records indicate precipitates and residues by underlining the formulas, and gases by overscoring.

THE GROUPING OF THE ELEMENTS

The Periodic Arrangement of the Elements. The selection of suitable reactions for carrying out the necessary separations and identifying tests involved in qualitative analysis is based on the properties of the elements concerned. An arrangement of the chemical elements into groups according to the variation of their properties with their atomic weights is given by the periodic table of the elements, page 115. Such a table is here reproduced to refresh the student's memory and place before him the elements to be studied. According to the periodic arrangement the elements toward the left of the table are the basic elements, which form the typical hydroxides; they are metallic in character and when in solution are free positive ions. The elements occupying the middle columns are less basic in character and may even show acidic properties; these are the typically amphoteric elements. To the right of the table are the elements showing strongly acid properties, which form the strong acids and in solution exist as anions. There are, of course, many exceptions to the general way in which the compounds of these elements ionize with respect to their position in the table.

Cations. The elements studied in this course are printed in bold-face type in the table. Those which ionize as cations and are studied in the schemes for cation analysis are the following, listed from their positions in the periodic table:

* A Laboratory Record Book has been prepared by the author and is published by John Wiley & Sons, Inc.

TABLE IX

Periodic Classification of the Elements

Group	I	II	III	IV	V	VI	VII	Transition Elements	VIII
Type Formulas	$R_2O—RH$	$RO—RH_2$	$R_2O_3—RH_3$	$RO_2—RH_4$	$R_2O_5—RH_3$	$RO_3—H_2R$	$R_2O_7—HR$		Inert gases
Series 1	**H 1.0081** 1								He 4.003
2	Li 6.940	Be 9.02	**B 10.82**	**C 12.010**	**N 14.008**	**O 16.0000**	**F 19.00**		Ne 20.183
3	**Na 22.997**	**Mg 24.32**	**Al 26.97**	**Si 28.06**	**P 30.98**	**S 32.06**	**Cl 35.457**		A 39.944
4	**K 39.096**	**Ca 40.08**	Sc 45.10	Ti 47.90	V 50.95	**Cr 52.01**	**Mn 54.93**	**Fe (55.84), Co (58.94), Ni (48.69)**	
5	**Cu 63.57**	**Zn 65.38**	Ga 69.72	Ge 72.60	**As 74.91**	Se 78.96	**Br 79.916**		Kr 83.7
6	Rb 85.48	**Sr 87.63**	Y 88.92	Zr 91.22	Cb 92.91	Mo 95.95	At. No. 43	Ru (101.7), Rh (102.91), Pd (106.7)	
7	**Ag 107.880**	**Cd 112.41**	In 114.76	**Sn 118.70**	**Sb 121.76**	Te 127.61	**I 126.92**		Xe 131.3
8	Cs 132.91	**Ba 137.36**	La* 138.92	Hf 178.6 (4)-10-2	Ta 180.88 (4)-11-2	W 183.92 (4)-12-2	Re 186.31 (4)-13-2	Os (190.2), Ir (193.1), Pt (195.23)	
9	Au 197.2	**Hg 200.61**	Tl 204.39	**Pb 207.21**	**Bi 209.00**	At. No. 84	At. No. 85		Rn 222
10	At. No. 87	Ra 226.05	At. No. 89	Th 232.12	Pa 231	U 238.07			

The atomic weight follows the symbol; only those elements included in the International Table are shown.
The elements in **bold-face type** are considered in the schemes of analysis.
* Fourteen other rare-earth metals occupy this same position.

The alkali metals, **sodium** (Na^+); **potassium** (K^+).

Copper in cupric salts (Cu^{++}); **silver** (Ag^+).

The alkaline earth metals, **magnesium** (Mg^{++}); **calcium** (Ca^{++}); **strontium** (Sr^{++}); **barium** (Ba^{++}).

Zinc (Zn^{++}); **cadmium** (Cd^{++}); **mercury in mercurous salts** (Hg_2^{++}) and in **mercuric salts** (Hg^{++}).

Aluminum (Al^{+++}).

Lead (Pb^{++}); **tin in stannous salts** (Sn^{++}) and in **stannic salts** (Sn^{++++}).

Arsenic in arsenious salts (As^{+++} and AsO_2^-) and in **arsenic salts** (As^{+++++}, and $AsO_4^{\equiv}$) **antimony** (Sb^{+++} and Sb^{+++++}); **bismuth** (Bi^{+++}).

Nitrogen in the form of the ammonium radical (NH_4^+).

Chromium in chromic salts (Cr^{+++}).

Manganese in manganous salts (Mn^{++}).

Iron in ferrous salts (Fe^{++}) and in **ferric salts** (Fe^{+++}); **nickel** (Ni^{++}); and **cobalt** (Co^{++}).

Anions. The elements which are considered under Anion Analysis in the form of their acid radicals are:

The halogens, **fluorine, chlorine, bromine** and **iodine** in **fluorides** (F^-); **chlorides** (Cl^- **and chlorates,** ClO_3^-); **bromides** (Br^-); **iodides** (I^-).

Sulfur in the form of **sulfides** ($S^=$); **sulfites** ($SO_3^=$); **thiosulfates** ($S_2O_3^=$); and **sulfates** ($SO_4^=$).

Chromium in chromates ($CrO_4^=$) and in **dichromates** ($Cr_2O_7^=$).

Nitrogen in nitrites (NO_2^-) and in **nitrates** (NO_3^-).

Phosphorus in **phosphates** ($PO_4^{\equiv}$).

Arsenic in **arsenites** (AsO_2^-) and in **arsenates** ($AsO_4^{\equiv}$).

Carbon in carbonates ($CO_3^=$) and in the organic radicals; viz., **oxalates** ($C_2O_4^=$), **acetates** ($C_2H_3O_2^-$) and **tartrates** ($C_4H_4O_6^=$).

Silicon in silicates ($SiO_3^=$).

Boron ($B_4O_7^=$, BO_2^-, $BO_3^{\equiv}$).

To this list are added the cyanogen radicals: **thiocyanates** (CNS^-), **ferricyanides** [$Fe(CN)_6^{\equiv}$], **ferrocyanides** [$Fe(CN)_6^{\equiv-}$], and **cyanides** (CN^-).

THE ANALYTICAL GROUPING OF THE CATIONS

Although the periodic table is a very useful arrangement of the elements and in many respects a most valuable guide in analytical chemistry, its application to the qualitative schemes is somewhat limited. For the purposes of qualitative analysis the cations and anions are arranged according to their behavior toward *certain specific reagents* used under carefully regulated conditions. The grouping of the cations into five groups is worked out in the following set of experiments. The analytical grouping of the anions is given in Part III.

The test solutions of the cations are of known strength and are made up so that each milliliter of each test solution contains 10

milligrams of the cation. A table of these test solutions is given in the Appendix, page 328. The nitrates of the metals have been used whenever possible because all nitrates are soluble in water and thus certain troublesome interferences with anions are avoided during the analysis of the cations.

Experiment 1. Take about 2 ml. of each of the test solutions, place in separate test tubes and add a few drops of dilute HCl to each tube. Precipitates of AgCl, Hg_2Cl_2 and $PbCl_2$ will form in the solutions containing silver, mercurous mercury and lead ions. Write the ionic equations taking place and make a note of the color and appearance of the precipitates formed. The other solutions will be unaffected by the reagent. The cations Ag^+, Hg_2^{++}, and Pb^{++} therefore constitute **Group I,** known as the **hydrochloric acid group** or the **silver group.** Save the acidified solutions with the exception of silver and mercury for the following experiments.

Experiment 2. Into each of the test solutions [with the exception of $AgNO_3$ and $Hg_2(NO_3)_2$], acidified with HCl from the foregoing experiment, pass a stream of H_2S gas. Sulfides, namely, HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3 and SnS, will be precipitated by the sulfide ion, $S^=$, in the presence of HCl, from the solutions containing Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++}, Sb^{+++} and Sn^{++}. The last three elements, if present in their higher states of oxidation as pentavalent arsenic, pentavalent antimony and tetravalent (stannic) tin, will be precipitated as As_2S_5, Sb_2S_5, and SnS_2. The above cations therefore constitute **Group II,** called the **hydrogen sulfide group** or the **copper and tin group.** Lead is included in this group because $PbCl_2$ is not completely precipitated by HCl in Group I. The element mercury when in the mercurous form will precipitate as the insoluble mercurous chloride (in Group I) but when in the mercuric form it will be precipitated as mercuric sulfide in this group. Hence mercury will be found in either group, depending on its state of oxidation. Make a notebook record of color and other characteristics of the above sulfides and write the ionic equations for the reactions taking place.

Experiment 3. Add a few crystals of NH_4Cl to the test solutions which remained unaffected by the above treatment; then add dilute NH_4OH to make them distinctly ammoniacal. The H_2S already present in the solutions will form $(NH_4)_2S$ and will precipitate Co^{++}, Ni^{++}, Fe^{+++}, Mn^{++} and Zn^{++} as CoS, NiS, Fe_2S_3, MnS and ZnS, and Al^{+++} and Cr^{+++} as $Al(OH)_3$ and $Cr(OH)_3$. These

DIAGRAMMATIC GROUPING OF THE CATIONS

To 2 ml. of each test solution add a few drops of dilute HCl

Solutions of:	*Precipitates:*	
Ag^+	$\underline{AgCl}$ (white)	Group I — The Hydrochloric Acid Group
Hg_2^{++}	$\underline{Hg_2Cl_2}$ (white)	
Pb^{++}	$\underline{PbCl_2}$ (white)	

(HCl) Pass in H_2S

Solutions of:	*Solutions of:*	*Precipitates:*	
Hg^{++}	Hg^{++}	$\underline{HgS}$ (black)	Group II — The Hydrogen Sulfide Group
$[Pb^{++}]$	Pb^{++}	$\underline{PbS}$ (black)	
Bi^{+++}	Bi^{+++}	$\underline{Bi_2S_3}$ (black)	
Cu^{++}	Cu^{++}	$\underline{CuS}$ (black)	
Cd^{++}	Cd^{++}	$\underline{CdS}$ (yellow)	
As^{+++}	As^{+++}	$\underline{As_2S_3}$ (yellow)	
As^{+5}	As^{+5}	$\underline{As_2S_5}$ (yellow)	
Sb^{+++}	Sb^{+++}	$\underline{Sb_2S_3}$ (orange)	
Sb^{+5}	Sb^{+5}	$\underline{Sb_2S_5}$ (orange)	
Sn^{++}	Sn^{++}	$\underline{SnS}$ (brown)	
Sn^{++++}	Sn^{++++}	$\underline{SnS_2}$ (yellow)	

Add NH_4Cl, NH_4OH and pass in H_2S

Solutions of:	*Solutions of:*	*Solutions of:*	*Precipitates:*	
Ni^{++}	Ni^{++}	Ni^{++}	$\underline{NiS}$ (black)	Group III—The Ammonium Sulfide Group
Co^{++}	Co^{++}	Co^{++}	$\underline{CoS}$ (black)	
Fe^{++}	Fe^{++}	Fe^{++}	$\underline{FeS}$ (black)	
Fe^{+++}	Fe^{+++}	Fe^{+++}	$\underline{Fe_2S_3}$ (black)	
Mn^{++}	Mn^{++}	Mn^{++}	$\underline{MnS}$ (pink)	
Al^{+++}	Al^{+++}	Al^{+++}	$\underline{Al(OH)_3}$ (white)	
Cr^{+++}		Cr^{+++}	$\underline{Cr(OH)_3}$ (green)	
Zn^{++}	Zn^{++}	Zn^{++}	$\underline{ZnS}$ (white)	

Add $(NH_4)_2CO_3$

Solutions of:	*Solutions of:*	*Solutions of:*	*Solutions of:*	*Precipitates:*	
Ba^{++}	Ba^{++}	Ba^{++}	Ba^{++}	$\underline{BaCO_3}$	Group IV—The Ammonium Carbonate Group
Sr^{++}	Sr^{++}	Sr^{++}	Sr^{++}	$\underline{SrCO_3}$	
Ca^{++}	Ca	Ca^{++}	Ca^{++}	$\underline{CaCO_3}$	

Solutions of:	*Solutions of:*	*Solutions of:*	*Solutions of:*	*Solutions of:*	
Mg^{++}	Mg^{++}	Mg^{++}	Mg^{++}	K^+	Group V—The Soluble Cation Group
K^+	K^+	K^+	K^+	NH_4^+	
Na^+	Na^+	Na^+	Na^+		
NH_4^+	NH_4^+	NH_4^+	NH_4^+		

cations, therefore, which precipitate as sulfides and hydroxides in ammoniacal solutions containing a high concentration of $S^{=}$ ions make up **Group III.** This is the **ammonium sulfide group** or the **iron and aluminum group.** Record the results in your notebook, together with the equations for the reactions.

Experiment 4. Boil off the H_2S from the remaining test solutions and add $(NH_4)_2CO_3$ reagent. **Ba^{++}, Sr^{++}, Ca^{++}** ions will be precipitated as $BaCO_3$, $SrCO_3$ and $CaCO_3$. These comprise **Group IV**, the **ammonium carbonate group** or the **alkaline earth group.**

The remaining test solutions, namely $\mathbf{Mg^{++}}$, $\mathbf{K^+}$, $\mathbf{Na^+}$ and $\mathbf{NH_4^+}$, which have not been precipitated by the preceding group reagents, are grouped together and called the **soluble cation group** or sometimes the **alkali group** (Group V).

Magnesium ions have been hindered from precipitating through the addition of NH_4Cl in Groups III and IV. The ammonium ion in the systematic analysis must be tested for in a portion of the original sample. It is included in this group because in its reactions and properties it resembles potassium.

This separation into analytical groups is shown in schematic form on page 118. Such diagrammatic schemes are used throughout the book to summarize briefly the procedures followed. In these schemes precipitates are indicated by underscoring and gases by overscoring. Test substances in solution are as a rule indicated as ions.

THE HYDROCHLORIC ACID GROUP — GROUP I

SILVER, Ag^+
MERCURY, Hg_2^{++}
LEAD, Pb^{++}

In a systematic separation of the cations into analytical groups, the first precipitating reagent used is hydrochloric acid, which precipitates $AgCl$, Hg_2Cl_2 and $PbCl_2$. These three chlorides are the only ones which are insoluble in cold water and dilute HCl. If, therefore, dilute HCl is added to a solution of metallic ions, the three chlorides, $AgCl$, Hg_2Cl_2 and $PbCl_2$, will be precipitated and all other cations will remain in solution. Owing to the appreciable solubility of $PbCl_2$, some lead will escape precipitation and consequently this ion is also included as a member of the next group.

The following preliminary experiments, by which the separation and identification of these three ions are carried out, are based on their properties. These analytical properties must be thoroughly understood and the experimental results correctly interpreted before an intelligent analysis can be made.

SILVER, Ag^+

Silver is a monovalent element. The oxide, Ag_2O, is formed rather than the hydroxide, when a silver solution is treated with NaOH or KOH:

$$2Ag^+ + 2OH^- = \underline{Ag_2O} + H_2O$$

Ammonium hydroxide likewise produces the oxide, which is soluble in an excess of ammonia:

$$\underline{Ag_2O} + 4NH_3 + H_2O = 2Ag(NH_3)_2^+ + 2OH^-$$

forming the complex diammono-silver ion.

Most of the salts of silver are insoluble in water. The nitrate and fluoride and, to a certain extent, the nitrite, sulfate, chlorate and acetate are water-soluble. Silver nitrate is a widely used reagent, frequently employed in analytical procedures as, for example, in the precipitation of anions.

Silver chloride is precipitated as a curdy white solid when hydrochloric acid or any soluble chloride is added to a solution containing Ag^+. The equation is:

$$Ag^+ + Cl^- = \underline{AgCl}$$

Sunlight will cause silver chloride to darken. AgCl is insoluble in dilute acids but somewhat soluble in concentrated HCl. It is soluble in ammonia solution, forming the complex ion, $Ag(NH_3)_2^+$. The equation for the reaction is:

$$\underline{AgCl} + 2NH_3 = Ag(NH_3)_2^+ + Cl^-$$

If a solution containing the complex ion is neutralized with dilute HNO_3, AgCl reprecipitates:

$$Ag(NH_3)_2^+ + Cl^- + 2H^+ = \underline{AgCl} + 2NH_4^+$$

The reprecipitation of AgCl from such an ammoniacal solution constitutes the test for silver.

AgCl is also soluble in potassium cyanide and in sodium thiosulfate solutions and is transformed into Ag_2S by ammonium polysulfide. With KCN, complex silver cyanide ions form:

$$\underline{AgCl} + 2CN^- = Ag(CN)_2^- + Cl^-$$

With $Na_2S_2O_3$, the " hypo " of the photographer, complex silver thiosulfate ions are produced. The reaction is probably:

$$\underline{2AgCl} + 3S_2O_3^{=} = Ag_2(S_2O_3)_3^{\equiv\equiv} + 2Cl^-$$

Silver bromide is somewhat more insoluble in water and in ammonia than AgCl. Silver iodide is still more insoluble in water than the other two halides and completely insoluble in ammonia.

This relationship will later be utilized in the detection of the chloride, bromide and iodide ion.

Hydrogen sulfide precipitates black silver sulfide, Ag_2S, from solutions of Ag^+. Since H_2S is the precipitating agent for Group II and indirectly also for Group III, it is important that silver be precipitated as completely as possible as AgCl in Group I. Ag_2S is insoluble in HCl but dissolves in hot HNO_3.

Ammonium carbonate, the reagent used in precipitating the alkaline earth elements which constitute Group IV, will precipitate Ag_2O.

PRELIMINARY EXPERIMENTS

Note: Instructions for carrying out experiments with test solutions of the cations and anions studied in this book are given under the heading "Preliminary Experiments." These experiments form the basis for the separation and identification of the ion in question. Record in your notebook a description of the products formed in all experiments performed, answer all questions and write balanced equations for all reactions.

1. Precipitation of Silver Chloride. To 5 ml. of the $AgNO_3$ test solution add dilute HCl dropwise until a precipitate no longer forms. Write the ionic equation for the reaction that takes place. Reserve the precipitate for further experiments. Determine whether NaCl and NH_4Cl produce the same precipitate. Why is HCl used rather than NH_4Cl?

Allow the precipitated AgCl to settle and pour off and discard the supernatant liquid. Add a few milliliters of water to the AgCl and heat the mixture. Does the precipitate appear to dissolve to any appreciable extent in hot water? This property of AgCl is used to separate AgCl (and mercurous chloride) from $PbCl_2$ (the latter salt is soluble in hot water).

2. Reaction of AgCl with NH_4OH. Decant the hot water and gradually add to the AgCl a dilute solution of NH_4OH. What happens? Explain the result. Write the reaction for the dissolving of AgCl in NH_3. This property of AgCl is used to separate silver chloride from mercurous chloride. The latter reacts in an entirely different way with this reagent.

3. Reprecipitation of AgCl and Test for Silver. Gradually add dilute HNO_3 to the test tube containing the $Ag(NH_3)_2^+$ until the solution is acid, stirring the solution and withdrawing a drop from

time to time with a glass rod and touching it to a piece of blue or neutral litmus paper. What happens when the solution is rendered acid? Give the equation.

MERCUROUS MERCURY, Hg_2^{++}

The element mercury forms two series of compounds, namely, the mercurous, such as the oxide, Hg_2O, the chloride and the nitrate, in which the element is monovalent, and the mercuric, in which mercury is divalent. In mercurous salts, the element is present in the form of the divalent group, Hg—Hg, written Hg_2^{++}, rather than as a single monovalent charged atom, Hg^+. In mercuric salts mercury is present as the divalent mercuric ion, Hg^{++}.

Mercurous chloride, Hg_2Cl_2 (calomel), is insoluble in water and dilute HCl; on the other hand, mercuric chloride, $HgCl_2$ (corrosive sublimate), is soluble in water and dilute acids. For this reason, the mercurous ion belongs in this analytical group and the mercuric ion is a member of the following group.

When a solution containing the mercurous ion, such as the test solution of $Hg_2(NO_3)_2$ is treated with a soluble chloride such as HCl or NH_4Cl, insoluble, white Hg_2Cl_2 is formed:

$$Hg_2^{++} + 2Cl^- = \underline{Hg_2Cl_2}$$

This salt is insoluble, like AgCl, in hot water. It reacts with NH_4OH to produce a mixture of black, metallic mercury and white, mercuric amido chloride, $HgNH_2Cl$. This is an internal redox reaction; one atom of mercurous mercury is reduced to Hg and the other is oxidized to the mercuric state. The equation is developed on page 133; in final form it is:

$$\underline{Hg_2Cl_2} + 2NH_4^+ + 2OH^- = \underline{HgNH_2Cl} + \underline{Hg} + 2H_2O + NH_4^+ + Cl^-$$

Metallic mercury, when acted upon by aqua regia, forms the weakly ionized salt, mercuric chloride, $HgCl_2$. The equation, balanced in detail on page 133, is:

$$\underline{3Hg} + 8H^+ + 2NO_3^- + 6Cl^- = 3HgCl_2 + \overline{2NO} + 4H_2O$$

Aqua regia also dissolves mercuric amido chloride, likewise with the formation of $HgCl_2$; the other products of the reaction

are NO, nitrogen and water. The reaction (see page 133) is:

$$2HgNH_2Cl + 4H^+ + 2NO_3^- + 2Cl^- = 2HgCl_2 + \overline{2NO} + N_2 + 4H_2O$$

Mercurous sulfide is at first formed when H_2S is passed into a solution containing the mercurous ion. The product, however, soon decomposes into a mixture of Hg and HgS.

Ammonium carbonate forms, with mercurous nitrate solution, a mixture of mercuric amido nitrate, mercuric oxide and free mercury.

The identifying test for mercury in this group consists of the reduction of mercuric chloride, formed as previously described by the action of aqua regia on Hg and $HgNH_2Cl$. The reducing agent is stannous chloride. When this reagent reacts on $HgCl_2$ the product first formed is Hg_2Cl_2. The reaction is:

$$2HgCl_2 + Sn^{++} + 2Cl^- = \underline{Hg_2Cl_2} + Sn^{++++} + 4Cl^-$$

A further reduction takes place, forming free mercury:

$$\underline{Hg_2Cl_2} + Sn^{++} + 2Cl^- = \underline{2Hg} + Sn^{++++} + 4Cl^-$$

The test appears as a white precipitate, gradually becoming gray owing to the mixture of Hg_2Cl_2 and Hg, or sometimes almost black if the reduction to Hg is complete.

PRELIMINARY EXPERIMENTS

1. Precipitation of Mercurous Chloride, Hg_2Cl_2. Add dilute HCl to 5 ml. of $Hg_2(NO_3)_2$ test solution until precipitation is complete. Write the equation for the reaction.

Decant as much of the supernatant liquid as possible from the precipitate, add a little water and heat the mixture. Does the precipitate dissolve in hot water? Compare the action of hot water here with that on AgCl, and bear this in mind when a similar experiment with $PbCl_2$ is performed. The difference in the action is used to separate AgCl and Hg_2Cl_2 from $PbCl_2$.

2. Reaction of Hg_2Cl_2 with NH_4OH. Filter off the precipitate of Hg_2Cl_2 and treat it with dilute ammonia solution. Does it dissolve? Is there any apparent change? Show how the equation for the reaction is balanced. Compare the effect of NH_4OH on Hg_2Cl_2 with its effect on AgCl.

3. Dissolving the "Black Residue." Remove some of the black mixture of Hg and $HgNH_2Cl$ and place it in a small evaporating dish. Prepare a small quantity of aqua regia by mixing three volumes of concentrated HCl with one volume of concentrated HNO_3 and add 5 ml. of this solvent to the residue. Under the hood, heat the mixture until the solution is nearly evaporated to dryness. Show by separate equations how aqua regia dissolves mercury and mercuric amido chloride. Refer to page 133 for the balancing of these equations. The almost complete evaporation of the solution is necessary to decompose the excess of reagent and to remove the chlorine produced in the decomposition of the aqua regia. When aqua regia decomposes, the products are Cl_2, NOCl and water. The reaction is:

$$NO_3^- + 3Cl^- + 4H^+ = Cl_2 + NOCl + 2H_2O$$

The presence of mercury can now be demonstrated in the almost completely evaporated solution by the following experiment.

4. Stannous Chloride Test for Mercury. Dilute the solution with 5 ml. of water and add, dropwise, a solution of stannous chloride. Observe how the precipitate gradually changes color. What is first formed? To what is the darkening due? Supply the equations for the reactions taking place.

LEAD, Pb^{++}

Lead forms two series of compounds, in which the element is respectively divalent and tetravalent. Thus, from the monoxide, litharge, PbO, are obtained the common salts such as $Pb(NO_3)_2$, $PbCl_2$, and $PbSO_4$. The hydroxide, $Pb(OH)_2$, is precipitated from Pb^{++} solutions by NaOH; it is an amphoteric substance, reacting with acids to give Pb^{++} ions and with bases to give the plumbite ion, $PbO_2^{=}$. The dioxide, PbO_2, is typical of the tetravalent compounds of lead. In the reactions utilized in the separation and detection of lead, only the divalent forms are involved.

Most of the salts of lead are insoluble in water, the notable exceptions being the nitrate, nitrite and acetate. Lead chloride is somewhat soluble in cold water and quite soluble in hot water. The bromide and iodide are less soluble in cold water than the chloride. Owing to the partial solubility of $PbCl_2$ in cold water, lead is not completely precipitated as lead chloride in this group.

The properties of lead which are involved in this group are here given; further properties of lead are considered on page 136.

The important salts of lead from an analytical standpoint are $PbCl_2$, $PbCrO_4$, $PbSO_4$ and PbS. The properties of the sulfate and sulfide are described on page 137.

Lead chromate is readily precipitated by K_2CrO_4 as a rather insoluble yellow salt. It is insoluble in acetic acid and in NH_4OH. This is the most characteristic test for lead.

PRELIMINARY EXPERIMENTS

1. Precipitation of Lead Chloride, $PbCl_2$. To 5 ml. of $Pb(NO_3)_2$ test solution add dilute HCl. Write the ionic equation for the reaction.

Decant, add 3 ml. of water and heat to boiling. How does the action here differ from that for AgCl and Hg_2Cl_2? Allow the solution to cool. What are the needle-like crystals which form?

2. Chromate Test for Lead. Warm the solution again to dissolve the crystals and divide the solution into two parts. To one portion add a few drops of potassium chromate, K_2CrO_4, reagent. Write the equation.

3. Sulfate Test for Lead. To the other portion of the lead chloride solution add dilute H_2SO_4. Note the nature of the precipitate. Write the equation. This is another good test for lead. Further properties of $PbSO_4$ are described on page 137.

REVIEW EXERCISES — SET 10

1. How may lead, silver and mercurous mercury ions be separated from all other common cations? Give the ionic equations for the reactions involved.

2. What property of lead can be used to separate it from silver and mercurous mercury? Does the separation of lead from silver involve a chemical reaction?

3. In experiment 1 under lead, what would have been the result if HCl had been added to a hot test solution of $Pb(NO_3)_2$?

4. What properties of the compounds of silver, lead and mercury suggest themselves as identifying tests for these cations?

5. What difference in behavior do AgCl and Hg_2Cl_2 show toward NH_4OH? Write the reactions. Does this suggest a method of separation?

6. What reaction is involved when $Ag(NH_3)_2Cl$ is treated with HNO_3? Write the equation.

7. What is the composition of the black precipitate formed by treating Hg_2Cl_2 with NH_4OH? Write the reactions between aqua regia and this residue.

8. The test solution of $Pb(NO_3)_2$ contains 10 milligrams of lead per milliliter. Calculate (*a*) the gram-atoms of Pb per liter and (*b*) the gram-moles of $Pb(NO_3)_2$ per liter.

9. Calculate the grams of hydrogen chloride required to precipitate, as AgCl, the Ag^+ contained in 5 ml. of test solution. (The student test solution will contain 10 milligrams per milliliter.) What weight of AgCl will be produced in the reaction?

10. What volume of dilute HCl solution (specific gravity 1.100) will be required to precipitate, as Hg_2Cl_2, 50 milligrams of Hg_2^{++} ion?

Outline of the Method of Analysis of this Group

The foregoing experiments have shown:

1. That AgCl, Hg_2Cl_2 and $PbCl_2$ are precipitated by dilute HCl. Reference to the group precipitation experiments, page 117, reveals that all other chlorides are soluble; hence through the formation of insoluble chlorides the members of this group can be separated from other cations.

2. That $PbCl_2$ is very soluble in hot water; AgCl and Hg_2Cl_2 are not. This property therefore serves to separate lead from silver and mercurous mercury. The presence of lead can be shown by the precipitation of yellow $PbCrO_4$ or white $PbSO_4$.

3. That AgCl is soluble in NH_4OH, whereas Hg_2Cl_2, although undergoing a change, is insoluble in this reagent. Ammonium hydroxide is therefore used to separate AgCl from Hg_2Cl_2. If the solution of the complex salt, $Ag(NH_3)_2Cl$, formed when AgCl dissolves in NH_4OH, is neutralized by HNO_3, AgCl is reprecipitated; this constitutes the test for silver. The product formed by the action of NH_4OH on Hg_2Cl_2 is a black mixture consisting of metallic mercury and mercuric amido chloride, $HgNH_2Cl$. Both constituents can be dissolved in aqua regia, and the test for mercury consists of reducing the resulting mercuric ion with stannous chloride.

These reactions and properties furnish the basis for the scheme of analysis and, when properly applied, the cations of this group can thus be separated and identified. The order of introducing the reagents and of conducting the various manipulations is shown diagrammatically in the scheme. This condensed arrangement, although it serves as a guide to the essential steps in the analysis, should by no means be employed as a set of working directions. The detailed procedure to be followed in the separation and detection of a mixture of these ions is here given.

DIAGRAMMATIC SCHEME — GROUP I

Solution:		*Precipitate:*		*Residue:*		*Residue:*
Hg_2^{++}		$\underline{Hg_2Cl_2}$		$\underline{Hg_2Cl_2}$		$\underline{HgNH_2Cl} + \underline{Hg}$ — Dissolved in aqua regia, boiled, $SnCl_2$ added; white, gray or black precipitate proves Hg.
Ag^+	Diluted to 25 ml. HCl added until precipitation is complete. Decanted through filter. Washed.	$\underline{AgCl}$	Boiled with 15 ml. water; filtered.	$\underline{AgCl}$	Treated with dilute NH_4OH; filtered.	*Filtrate:* $Ag(NH_3)_2^+$ — Acidified with dilute HNO_3; white precipitate proves Ag.
Pb^{++}		$\underline{PbCl_2}$		*Filtrate:* Pb^{++}	K_2CrO_4 added; yellow precipitate proves Pb.	

Practice Analysis of a Mixture Containing Lead, Silver and Mercurous Mercury Ions

Preparation of Mixture. Prepare a mixture of the cations of this group by placing in a beaker about 15 ml. of the $Pb(NO_3)_2$ test solution, 5 ml. of the $AgNO_3$ test solution and 5 ml. of the $Hg_2(NO_3)_2$ test solution. This solution will be acid from the HNO_3 used in preparing the mercurous nitrate test solution, but the presence of not too large amounts of HNO_3 will not interfere with the group precipitation.

Group Precipitation. Take the 25 ml. portion of the sample just prepared and add dilute HCl slowly with constant stirring, until a precipitate no longer forms. Allow the precipitate to settle and to the clear supernatant solution add a drop or two of the dilute precipitating agent; if incomplete precipitation is indicated by the formation of a white precipitate, continue the addition of HCl until precipitation is complete. The precipitate consists of a mixture of $PbCl_2$, AgCl and Hg_2Cl_2 and is formed by the simple combining of ions as shown in the equations:

$$Pb^{++} + 2Cl^- = \underline{PbCl_2}$$

$$Ag^+ + Cl^- = \underline{AgCl}$$

$$Hg_2^{++} + 2Cl^- = \underline{Hg_2Cl_2}$$

take place. The solution in which a precipitate has been formed contains just enough of the ions involved so that the product of their concentrations is equal to the $K_{s.p.}$ of that precipitate. The concentration of one ion may greatly exceed that of the other and, in fact, it is desirable to have an excess of the precipitating ions in order to insure more complete removal of the ions being precipitated.

The molar and gram solubilities and the solubility product constants of the chlorides of this group are given in the table below:

TABLE X

Substance	Solubility Grams per Liter	Solubility Moles per Liter	$K_{s.p.}$
Hg_2Cl_2	3.8×10^{-4}	8.0×10^{-7}	2.0×10^{-18}
AgCl	1.5×10^{-3}	1.06×10^{-5}	1.1×10^{-10}
$PbCl_2$	11.0	3.9×10^{-2}	2.4×10^{-4}

Note the small value for the $K_{s.p.}$ of Hg_2Cl_2, indicating it to be a very insoluble compound. $PbCl_2$, on the other hand, has a relatively large value. It is quite soluble; so much so that an appreciable amount of the lead escapes precipitation in this group.

The solubility product principle, as already pointed out, enables us to calculate the amount of precipitating reagent to add in order to initiate the precipitation of the desired ion. Thus, in a solution containing a known concentration of silver ion we can calculate the concentration of chloride ion necessary to give a precipitate of AgCl, according to the following equation:

$$C_{Ag^+} \times C_x = 1.1 \times 10^{-10}$$

where C_x is the required gram-ion concentration of chloride ion and 1.1×10^{-10} is the $K_{s.p.}$ of AgCl. Applying this equation to a solution containing a known concentration of Ag^+ ion, we can readily calculate the concentration of Cl^- ion required to saturate the solution, and any excess beyond this must result in the precipitation of AgCl. If, for example, a certain solution contains 1×10^{-2} gram-ion of Ag^+ per liter, from the equation:

$$1 \times 10^{-2} \times x = 1.1 \times 10^{-10}$$

the concentration of chloride ion is approximately 10^{-8} gram-ion.

The solubility product equation for Hg_2Cl_2 is expressed by the relation:

$$C_{Hg_2^{++}} \times (C_{Cl^-})^2 = K_{s.p.(2.0 \times 10^{-18})}$$

To find the chloride-ion concentration necessary to start the precipitation of Hg_2Cl_2 in a solution in which the mercurous-ion concentration has a definite known value, say 1×10^{-2}, it is necessary to solve for the chloride-ion concentration in the above equation.

$$(1 \times 10^{-2}) \times (x)^2 = 2.0 \times 10^{-18}$$

from which $x = 1.4 \times 10^{-8}$ gram-ion of Cl^-.

In the same way, in a solution of a lead salt containing this same concentration of Pb^{++} ion, the chloride-ion concentration required to start precipitation of $PbCl_2$ is obtained from the equation:

$$C_{Pb^{++}} \times (C_{Cl^-})^2 = K_{s.p.}$$

$$1 \times 10^{-2} \times (x)^2 = 2.4 \times 10^{-4}$$

from which $x = 0.16$ gram-ion of Cl^- ion.

Suppose a solution contains both Hg_2^{++} ions and Pb^{++} ions, each having a concentration of 1×10^{-2}. If chloride ions are added, the solution will become saturated with respect to Hg_2Cl_2 when the Cl^- ion concentration reaches 1.4×10^{-8}, and henceforth solid Hg_2Cl_2 will precipitate, unmixed with $PbCl_2$, until the solution becomes saturated with respect to $PbCl_2$ also; after this there will be simultaneous precipitation of both Hg_2Cl_2 and $PbCl_2$. The concentrations of Hg_2^{++} and Pb^{++} in the solution when the latter begins to precipitate can be determined from the principle of fractional precipitation discussed on page 70. The ratio of Pb^{++} to Hg_2^{++} is the same as the ratio of the solubility product constants of these two chlorides:

$$\frac{C_{Pb^{++}}}{C_{Hg_2^{++}}} = \frac{K_{s.p.(PbCl_2)}}{K_{s.p.(Hg_2Cl_2)}} = \frac{2.4 \times 10^{-4}}{2.0 \times 10^{-18}} = 1.1 \times 10^{14}$$

From this it follows that, when both chlorides are precipitating, the concentration of Pb^{++} ion in solution is enormously greater than that of the Hg_2^{++} ion.

Complex-Ion Formation. An application of the theory of complex ions is encountered in this group in the separation of silver from mercurous mercury. NH_4OH will dissolve $AgCl$ on account

of the formation of the complex silver ammonia ions, according to the reaction:

$$\underline{AgCl} + 2NH_3 = Ag(NH_3)_2^+ + Cl^-$$

This complex ion tends to dissociate into its simpler components thus:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

and an equilibrium is set up between these components which can be formulated by the equilibrium expression:

$$\frac{C_{Ag^+} \times (C_{NH_3})^2}{C_{Ag(NH_3)_2^+}} = K_{\text{(instability constant)}}$$

An excess of NH_3 will therefore force back the ionization and lower the concentration of Ag^+ ions. The Ag^+ ion concentration becomes so low that the $K_{s.p.}$ for AgCl is not exceeded, and consequently solid AgCl will continue to dissolve in order to maintain the required ion concentration. This cycle continues until the AgCl is completely dissolved. When HNO_3 is added to the solution containing the complex ion, its action is to neutralize the ammonia, thus disturbing the above equilibrium and precipitating AgCl.

Oxidation-Reduction. Redox phenomena are encountered in the separation and identification of mercury. The first case, that of the action of NH_4OH on Hg_2Cl_2, is an interesting example of an internal oxidation-reduction reaction in which one monovalent atom of mercury becomes oxidized to the mercuric state (forming $HgNH_2Cl$) at the expense of another which becomes reduced to the zero-valent (metallic) condition.

The writing of the equation for this reaction is not so readily apparent, hence will here be shown. The reduction of the mercurous chloride to metallic mercury can be shown by the half-cell equation:

$$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg^0 + 2Cl^-$$

two electrons being required to reduce Hg_2^{++} to $2Hg^0$; the oxidation of Hg_2Cl_2 to $HgNH_2Cl$ is written as the other half-cell reaction:

$$Hg_2Cl_2 + 4NH_4OH \rightleftharpoons 2HgNH_2Cl + 2e + 4H_2O + 2NH_4^+$$

the two electrons being lost by Hg_2^{++} in becoming $2Hg^{++}$.

Adding these two half-cell reactions and dividing the entire equation by 2 give:

$$Hg_2Cl_2 + 2NH_4OH = Hg + HgNH_2Cl + NH_4Cl + 2H_2O$$

The second case is the dissolving of this black mixture in aqua regia. Here we have:

(1) The oxidation of metallic Hg to $HgCl_2$:

$$3[Hg + 2Cl^- = HgCl_2 + 2e]$$

$$2[NO_3^- + 4H^+ + 3e = NO + 2H_2O]$$

giving:

$$3Hg + 8H^+ + 2NO_3^- + 6Cl^- = 3HgCl_2 + 2NO + 4H_2O$$

(2) The dissolving of $HgNH_2Cl$. The equation for the reaction can be balanced in the following manner. In the half-cell reaction:

$$2NH_2^- \rightleftharpoons N_2 + 4H^+ + 6e$$

the 6 electrons lost will reduce $2NO_3^-$ to 2NO:

$$2NO_3^- + 8H^+ + 6e \rightarrow 2NO + 4H_2O$$

The completed reaction is:

$$2HgNH_2Cl + 2Cl^- + 2NO_3^- + 4H^+ = 2HgCl_2 + N_2 + 2NO + 4H_2O$$

(3) The reduction of $HgCl_2$ by $SnCl_2$ successively to Hg_2Cl_2 and finally to Hg.

THE HYDROGEN SULFIDE GROUP — GROUP II

MERCURY, Hg^{++}	**ARSENIC, As^{+++} AsO_2^- and As^{+++++} $AsO_4^{\equiv}$**
LEAD, Pb^{++}	**ANTIMONY, Sb^{+++} and Sb $^{+++++}$**
BISMUTH, Bi^{+++}	**TIN, Sn^{++} and Sn^{++++}**
COPPER, Cu^{++}	
CADMIUM, Cd^{++}	

The cations of this group are those whose sulfides are precipitated by H_2S from solutions acidified with HCl. They are: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++} (AsO_2^-) and As^{+++++} ($AsO_4^{\equiv}$), Sb^{+++} and Sb^{+++++}, Sn^{++} and Sn^{++++}. Mercuric salts are not precipitated by HCl but mercurous salts are. This fact places mercuric mercury in this group and mercurous mercury in Group I. Lead is not completely precipitated by HCl, hence provision must be made in this group for its separation and detection.

Cupric copper and cadmium resemble each other closely in their analytical reactions. Arsenic, no matter whether occurring originally as trivalent or pentavalent cation or as the anions AsO_2^- or $AsO_4^{\equiv}$, will be precipitated as As_2S_3 and As_2S_5 by this group reagent. Antimony salts show a similar behavior. Tin may be present in the starting material as stannous or as stannic salts and will be precipitated as the corresponding sulfides, SnS and SnS_2.

The sulfides of this group are divided into two subgroups by the action of ammonium polysulfide, $(NH_4)_2S_x$. Those which remain practically insoluble in this reagent are HgS, PbS, Bi_2S_3, CuS and CdS. This subgroup is known as Division A or the " copper subgroup." The sulfides which are dissolved by ammonium polysulfide are As_2S_3 and As_2S_5, Sb_2S_3 and Sb_2S_5, SnS and SnS_2. This subgroup is known as Division B or the " tin subgroup."

During the systematic analysis of a mixture of ions of this and the following group, it is urgently important that correct conditions of acidity, concentration and temperature be maintained in order that the sulfides of this group are precipitated, and at the same time the sulfides of Group III are not precipitated. The theory here involved is discussed in detail on page 168. In brief, during the precipitation of this group, the acidity is kept at 0.3 *M*, requiring for this purpose 2.5 ml. of concentrated HCl per 100 ml. of solution; this is done in order that the sulfide-ion concentration can be controlled. In the procedures, therefore, for the preliminary experiments as well as the analysis of known and unknown mixtures, it is highly important to maintain carefully this acidity and to understand why this must be done.

The Ions of Division A, Group II

MERCURIC MERCURY, Hg^{++}

Mercuric salts, as a rule, are more soluble than the corresponding mercurous salts, although most of them are insoluble in water. The fact that mercuric chloride is soluble in water and dilute HCl places mercuric mercury in this group rather than in the preceding group. Many of the mercuric salts are poisonous. Mercuric salts, like the mercurous ones, show a tendency to hydrolyze in aqueous solution; the test solution of $Hg(NO_3)_2$, for example,

hydrolyzes to form the insoluble basic nitrate, $Hg(OH)NO_3$. To prevent its formation the test solution is kept strongly acid with HNO_3. A solution of $HgCl_2$ is very slightly ionized; this is an exception to the general behavior of salts. In the presence of a large excess of Cl^-, $HgCl_2$ forms a complex ion represented by the formula, $HgCl_4^=$.

The most important compound of mercuric mercury is the sulfide, HgS. When H_2S is passed into a solution containing the Hg^{++} ion there is formed at first a white precipitate which gradually changes color, finally becoming black. These color changes are due to varying proportions of double salts of HgS and $HgCl_2$, such as $HgS{\cdot}HgCl_2$. HgS is black, extremely insoluble in water and practically insoluble in dilute acids as well as in ammonium polysulfide. If HgS is boiled with dilute HNO_3 for some time, it will be transformed into a white, insoluble double salt, $Hg(NO_3)_2{\cdot}2HgS$.

Aqua regia is required to dissolve mercuric sulfide. The action of this solvent can best be understood by considering the reaction involved. The products formed in the reaction are the slightly ionized $HgCl_2$, free sulfur, NO and water. Like other reactions with aqua regia, this is a redox reaction. The balancing of the equation for the reaction is carried out as follows. As noted elsewhere, the constituent ions in aqua regia are NO_3^-, H^+ and Cl^-. For the half-cell reaction involving the reduction of NO_3^- to NO we have:

$$NO_3^- + 4H^+ + 3e = NO + 2H_2O \qquad (1)$$

The oxidation of the sulfide ion in HgS to free S is represented by:

$$S^= = S^0 + 2e \qquad (2)$$

This equation when combined with the formation of $HgCl_2$ gives:

$$HgS + 2Cl^- = S + HgCl_2 + 2e \qquad (3)$$

To balance the electrons, equation (1) is multiplied by 2 and equation (3) by 3. Adding these and canceling out the electrons gives:

$$2NO_3^- + 8H^+ + 6e = 2NO + 4H_2O$$

$$3HgS + 6Cl^- = 3S + 3HgCl_2 + 6e$$

$$3HgS + 6Cl^- + 2NO_3^- + 8H^+ = 3S + 2NO + 3HgCl_2 + 4H_2O$$

If desired, this ionic equation can easily be transformed into the following molecular one:

$$3HgS + 6HCl + 2HNO_3 = 3HgCl_2 + 3S + 2NO + 4H_2O$$

The test for mercury consists, as already described on pages 123 and 129, of the reduction of $HgCl_2$ by means of stannous chloride.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Mercuric Sulfide. To 5 ml. of mercuric nitrate, $Hg(NO_3)_2$, test solution add 2.5 ml. of concentrated HCl, dilute to 50 ml. and pass in H_2S. Account for the change in color of the precipitate. Write the equation for the formation of HgS.

Filter off and wash the precipitate. Use separate portions of the precipitate for the following experiments.

Action of Ammonium Polysulfide on HgS. To one portion of the precipitate, transferred to a test tube, add 2 ml. of ammonium polysulfide. This reagent, known also as yellow ammonium sulfide, is made by dissolving sulfur in a strong solution of ammonium sulfide; it contains several different kinds of sulfide ions, the disulfide $S_2^=$ and the monosulfide $S^=$ predominating. Its formula is variously given as $(NH_4)_2S_x$ or $(NH_4)_2S_2$. This reagent is used in the systematic scheme given in this book to separate the sulfides of this group into two subdivisions.

Does the HgS appear to dissolve in this reagent? Make a note of this property of HgS and later compare the action of this solvent on the other sulfides of this group.

Action of Dilute HNO_3 on HgS. Treat another portion of the HgS with dilute HNO_3. Heat the mixture gently at first. Does HgS dissolve? Continue boiling for some time. Account for any observed change in the precipitate.

Action of Aqua Regia on HgS. To a third portion of the precipitate add 5 ml. of aqua regia, and heat if necessary in order to dissolve it. Write the reaction showing the method of balancing the equation.

2. Review the test with $SnCl_2$ as described on page 124.

LEAD, Pb^{++}

The failure of HCl to completely precipitate lead as $PbCl_2$ in the preceding group makes it necessary to provide for its further

separation in this group. In fact, if the amount of lead in a sample is too small to give a precipitate with HCl, no separation as $PbCl_2$ in Group I is at all possible and small amounts of lead are consequently detected only in Group II. The sulfide, however, is very insoluble and enables one to precipitate lead almost completely as PbS. Properties relating to the sulfide and sulfate are given below.

Lead sulfide, PbS, is readily precipitated by H_2S from alkaline, neutral or slightly acid solutions containing the lead ion, as a ~~black, very insoluble substance. If~~ the acidity is too great PbS will either not precipitate or else there will be formed a reddish black double salt, $PbCl_2 \cdot 2PbS$.

The sulfide is insoluble in cold dilute acids and in ammonium polysulfide. Hot dilute HNO_3 will dissolve it with the formation of Pb^{++}, free sulfur and NO. In this respect it differs from HgS and shares this property with Bi_2S_3, CuS and CdS. The solubility of PbS in HNO_3 is accounted for by the oxidizing action of NO_3^- on the $S^{=}$ ion. The writing of the equation for this reaction is as follows: When PbS dissolves in warm dilute HNO_3 the products of the reaction are Pb^{++}, free S, NO and H_2O. To balance the equation:

$$\underline{PbS} + NO_3^- + H^+ = Pb^{++} + NO + S + H_2O$$

resolve it into two half-cell equations

$$S^{=} = S^0 + 2e$$

from which we have:

$$PbS = Pb^{++} + \underline{S} + 2e \qquad (1)$$

and

$$NO_3^- + 4H^+ + 3e = NO + 2H_2O$$

Multiplying, adding and canceling electrons gives the balanced equation in ionic form:

$$3PbS = 3Pb^{++} + 3S + 6e$$

$$2NO_3^- + 8H^+ + 6e = 2NO + 4H_2O$$

$$3PbS + 8H^+ + 2NO_3^- = 3Pb^{++} + 3S + 2NO + 4H_2O$$

Expressed in molecular form, since $8H^+$ require $8HNO_3$, the equation may be written thus:

$$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 3S + 2NO + 4H_2O$$

Lead sulfate, $PbSO_4$, is best precipitated by adding a large excess of H_2SO_4. It is soluble in ammonium acetate owing to the formation of the slightly ionized salt, $Pb(C_2H_3O_2)_2$:

$$\underline{PbSO_4} + 2C_2H_3O_2^- = Pb(C_2H_3O_2)_2 + SO_4^{=}$$

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Lead Sulfide, PbS. Dilute 5 ml. of $Pb(NO_3)_2$ test solution to 50 ml., add 2.5 ml. of concentrated HCl and saturate with H_2S. Write the ionic equation for the formation of PbS. Repeat the experiment, doubling the quantity of HCl. Explain the result.

Action of Ammonium Polysulfide on PbS. Filter off the PbS obtained in the first part of the above experiment and divide into two portions. To one portion add some ammonium polysulfide. Is there any apparent action?

Action of Dilute HNO_3 on PbS. Add dilute HNO_3 to the other portion of the precipitate and warm the mixture. How does the action differ from that of HgS? Write the equation, showing the steps involved in the balancing.

2. Properties of Lead Sulfate, $PbSO_4$. Add a few milliliters of dilute H_2SO_4 to lead nitrate test solution and evaporate until dense white fumes of SO_3 are evolved. Cool and pour the solution into cold water. The white precipitate is $PbSO_4$. Write the reaction. This is the method of separating lead from bismuth, copper and cadmium, since the sulfates of the latter three cations are soluble in water and dilute H_2SO_4.

Filter off the $PbSO_4$ and pour through the filter a few milliliters of hot dilute ammonium acetate, $NH_4C_2H_3O_2$, solution. Test for lead in the filtrate. How?

BISMUTH, Bi^{+++}

The common valences of bismuth are +3 and +5. The chief oxides are Bi_2O_3 and Bi_2O_5. The properties and reactions of only the trivalent ion, Bi^{+++}, are here considered. A characteristic property of bismuth salts is the ease with which they hydrolyze, precipitating insoluble basic salts. Thus the chloride readily hydrolyzes to the oxychloride, BiOCl; the nitrate first forms the oxynitrate, $BiONO_3$, which then passes over into the subnitrate $(BiO)_2(OH)NO_3$.

On account of the ease of hydrolysis, the test solution of $Bi(NO_3)_3$ is kept strongly acid with HNO_3 to prevent the precipitation of $BiONO_3$.

Bismuth hydroxide, $Bi(OH)_3$, a white solid, is formed when NH_4OH or NaOH is added to Bi^{+++}:

$$Bi^{+++} + 3OH^- = \underline{Bi(OH)_3}$$

It is insoluble in an excess of ammonia solution, differing in this respect from $Cu(OH)_2$ and $Cd(OH)_2$, the latter two dissolving to form complex ions. This property of $Bi(OH)_3$ serves to separate bismuth from copper and cadmium.

As already noted, solutions of bismuth salts, such as $BiCl_3$, readily hydrolyze. In the case of the chloride, by diluting with water we have:

$$Bi^{+++} + Cl^- + HOH \rightleftharpoons \underline{BiOCl} + 2H^+$$

This reaction is distinctly reversible and therefore if much acid is added to a solution containing precipitated BiOCl the latter dissolves. The formation of BiOCl is one of the tests for bismuth.

Bismuth sulfide, Bi_2S_3, a dark brown, very insoluble substance, is formed when H_2S or $(NH_4)_2S$ is added to a Bi^{+++} solution.

$$2Bi^{+++} + 3S^{=} = \underline{Bi_2S_3}$$

This sulfide is insoluble in ammonium polysulfide and in cold dilute acids, but readily dissolves in hot dilute HNO_3. The reaction can be expressed ionically by the equation:

$$\underline{Bi_2S_3} + 2NO_3^- + 8H^+ = 2Bi^{+++} + 3S + 2NO + 4H_2O$$

This equation is similar to the one given for PbS; the method of balancing was developed on page 137.

Sulfuric acid does not react with Bi^{+++} to form an insoluble sulfate.

Sodium stannite reduces Bi^{+++} or $Bi(OH)_3$ to black, metallic Bi. This is the best test for bismuth. The reagent is prepared, as needed, by treating a solution of $SnCl_2$ with an excess of NaOH. In the preparation of this reagent, the product which first forms is $Sn(OH)_2$ and this dissolves in an excess of the base, on account of its amphoteric nature, to form the stannite ion, $SnO_2^{=}$:

$$Sn^{++} + 2OH^- = \underline{Sn(OH)_2}$$

$$\underline{Sn(OH)_2} + 2OH^- = SnO_2^{=} + 2H_2O$$

When $Bi(OH)_3$ is treated with this reagent reduction of the bismuth to Bi takes place:

$$2Bi^{+++} + 6OH^- + 3SnO_2^{=} = \underline{2Bi} + 3SnO_3^{=} + 3H_2O$$

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Bismuth Sulfide, Bi_2S_3. Neutralize 5 ml. of $Bi(NO_3)_3$ test solution with dilute NH_4OH, add 2.5 ml. of concentrated HCl, dilute the solution to 100 ml. with water and pass in H_2S. Note the color of the precipitate and write the equation.

Action of Ammonium Polysulfide on Bi_2S_3. Decant the solution and treat the Bi_2S_3 with a few milliliters of $(NH_4)_2S_2$. Does it dissolve? Compare the action with that for HgS and PbS.

Action of Dilute HNO_3 on Bi_2S_3. Wash the undissolved precipitate with a small portion of water, filter and then pass through the filter 5 ml. of hot, dilute nitric acid. Show how the equation for the reaction is balanced by supplying the half-cell equations. Is this property of Bi_2S_3 like that of HgS and of PbS?

2. Action of H_2SO_4. Add dilute H_2SO_4 to a few milliliters of bismuth test solution. Does a precipitate of bismuth sulfate form? Compare this with the analogous experiment with lead.

3. Precipitation of $Bi(OH)_3$. To a few milliliters of $Bi(NO_3)_3$ test solution add dilute NH_4OH until a precipitate forms. Write the equation.

Add an excess of the reagent. Is $Bi(OH)_3$ soluble in an excess of NH_4OH?

4. Hydrolysis of Bismuth Chloride. Dissolve a portion of the $Bi(OH)_3$ obtained in experiment 3 by adding a small amount of dilute HCl, and then dilute the solution with a large volume of water. What forms? What is the equation for the reaction?

5. Sodium Stannite Test for Bismuth. Prepare some sodium stannite reagent by adding a solution of NaOH to a $SnCl_2$ solution until the $Sn(OH)_2$ which first forms redissolves. The reagent thus prepared contains the stannite ion, $SnO_2^{=}$, a good reducing agent.

To the remainder of the $Bi(OH)_3$ obtained in experiment 3 add some of the freshly prepared reagent. What happens? Write the redox reaction. This is a very sensitive test for bismuth.

COPPER, Cu^{++}

Copper forms two series of salts, the cuprous, in which copper is monovalent, and the cupric in which this element is divalent. Cuprous salts are easily oxidized to the cupric form; they are for the most part insoluble in water. The test solution is made from $Cu(NO_3)_2$, and therefore con ains the cupric ion, Cu^{++}. Cupric nitrate is derived by dissolving the black cupric oxide, CuO, in nitric acid.

Cupric hydroxide, $Cu(OH)_2$, a blue precipitate, is formed when a dilute solution of NaOH or KOH reacts with cupric ion.

The same product, or possibly a basic salt, is formed when an equivalent amount of dilute ammonia solution is added to Cu^{++}:

$$Cu^{++} + 2OH^- = \underline{Cu(OH)_2}$$

If an excess of the ammonia reagent is used, the precipitate dissolves forming the complex $Cu(NH_3)_4^{++}$ ion:

$$\underline{Cu(OH)_2} + 4NH_3 = Cu(NH_3)_4^{++} + 2OH^-$$

In the Werner system of nomenclature this complex of copper and ammonia is called the tetrammono-cupric ion. This complex has an intensely blue color and is one of the tests for copper.

Cupric sulfide, CuS, is formed when a cupric solution is treated with sulfide ion. The cupric sulfide is very insoluble and readily forms when H_2S is passed into a strongly acidified solution of Cu^{++}:

$$Cu^{++} + S^{=} = \underline{CuS}$$

This sulfide is soluble to a slight extent in ammonium polysulfide, forming the complex thio-ion $CuS_2^{=}$, so that the separation of copper from arsenic, antimony and tin is not perfect and traces of copper may consequently be found in Division B upon analysis of samples containing this element.

Dilute, hot nitric acid dissolves CuS with the formation of Cu^{++}, NO, S and water. The equation:

$$\underline{3CuS} + 2NO_3^- + 8H^+ = 3Cu^{++} + \overline{2NO} + \underline{3S} + 4H_2O$$

is balanced in the same way as developed for the action of HNO_3 on PbS (see page 137).

Cupric ion reacts with an excess of KCN to form a very stable complex. When a cupric solution is treated with KCN the first

result is the formation of cupric cyanide:

$$Cu^{++} + 2CN^{-} = \underline{Cu(CN)_2}$$

This immediately is reduced to cuprous cyanide:

$$2Cu(CN)_2 \rightarrow \underline{Cu_2(CN)_2} + (CN)_2$$

An excess of KCN then reacts, forming a colorless solution which contains the cuprocyanide complex ion:

$$\underline{Cu_2(CN)_2} + 6CN^{-} = 2Cu(CN)_4^{=}$$

From a solution containing this complex, H_2S will not precipitate Cu_2S. A corresponding but less stable complex is formed with Cd^{++}; this difference in stability of these two complexes is utilized to detect cadmium in the presence of copper.

A very sensitive test for copper is the reddish brown precipitate of cupric ferrocyanide which forms when potassium ferrocyanide is added to a cupric solution:

$$2Cu^{++} + Fe(CN)_6^{==} = \underline{Cu_2Fe(CN)_6}$$

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Cupric Sulfide, CuS. Add 2.5 ml. of concentrated HCl to 5 ml. of $Cu(NO_3)_2$ test solution, dilute to 100 ml. and saturate the solution with H_2S. Write the reaction. Note the color of the precipitate.

Action of Ammonium Polysulfide on CuS. Filter off the CuS and treat a portion of it with $(NH_4)_2S_2$, warming the mixture. Is CuS soluble in this reagent to any extent at all? If a small portion dissolves owing to prolonged action of the reagent. where further in the analytical scheme might copper be detected?

Action of Dilute HNO_3 on CuS. Treat the remainder of the CuS with hot, dilute HNO_3. Why is an oxidizing solvent necessary to dissolve sulfides like CuS? In this respect, CuS resembles what other sulfides? Show how the equation for the reaction is balanced.

2. Complex Ion of Copper and Ammonia. Add dilute ammonia solution to 5 ml. of test solution until a deep blue color develops. What is the complex formed? Write the equation. Compare the effect here with the action of NH_4OH on AgCl and on $Bi(OH)_3$.

3. Ferrocyanide Test for Copper. Add a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$, reagent to 1 ml. of copper test solution. Note the color and give the equation. This is a very sensitive test for copper.

4. Complex Ion of Copper and Cyanide. To 2 ml. of the $Cu(NH_3)_4^{++}$ solution obtained in experiment 2 add, dropwise, a dilute solution of KCN. *Caution: KCN is a violent poison! Work with extreme care. Perform the experiment under the hood.* Continue adding the reagent until the blue color of the solution is discharged. In what oxidation state is the copper now? Compare the stability of the complex with the corresponding one formed with cadmium. Write the equation, showing the steps in the reaction.

CADMIUM, Cd^{++}

Cadmium forms salts in which this element always has a valence of +2. Many of the salts of cadmium are insoluble in water. In its analytical reactions cadmium closely resembles copper. The sulfide and the complexes formed with ammonia ion and with cyanide ion are the most important forms from an analytical standpoint.

Cadmium sulfide, CdS, yellow, is formed when H_2S is passed into a neutral, alkaline or acid solution containing Cd^{++}.

$$Cd^{++} + S^{=} = \underline{CdS}$$

If the acidity is somewhat high, precipitation of the sulfide may be incomplete and there may be formed an orange-colored precipitate of a double salt of the probable composition, $CdCl_2 \cdot CdS$. In slightly acid solutions, the precipitation of CdS is practically complete.

CdS is insoluble in ammonium polysulfide, sharing this property in common with HgS, PbS, Bi_2S_3 and for the most part with CuS. It dissolves in hot, dilute HNO_3:

$$\underline{3CdS} + 2NO_3^- + 8H^+ = 3Cd^{++} + \overline{2NO} + \underline{3S} + 4H_2O$$

Like the cupric ion, Cd^{++} reacts with NH_4OH first to precipitate the hydroxide:

$$Cd^{++} + 2OH^- = \underline{Cd(OH)_2}$$

The hydroxide is soluble in an excess of the reagent forming the

colorless complex ion, $Cd(NH_3)_4^{++}$:

$$\underline{Cd(OH)_2} + 4NH_3 = Cd(NH_3)_4^{++} + 2OH^-$$

corresponding to the deep blue tetrammono-cupric complex.

The cadmium ion reacts with an equivalent amount of potassium cyanide to form cadmium cyanide:

$$Cd^{++} + 2CN^- = \underline{Cd(CN)_2}$$

This dissolves in an excess of CN^-, forming a complex cadmium-cyanide ion:

$$Cd(CN)_2 + 2CN^- = Cd(CN)_4^{=}$$

This ion is much less stable than the cuprocyanide complex formed with copper, and this difference in stability enables one to detect cadmium in the presence of copper for, if H_2S is passed into a solution containing both $Cu(CN)_4^{\equiv}$ and $Cd(CN)_4^{=}$, cadmium sulfide only will be precipitated, the great stability of $Cu(CN)_4^{\equiv}$ suppressing the concentration of cuprous ions to such an extent that Cu_2S cannot form and, by its black color, obscure the yellow color of CdS.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Cadmium Sulfide, CdS. To 5 ml. of $Cd(NO_3)_2$ test solution add 2.5 ml. of concentrated HCl, dilute to 50 ml., heat to boiling and pass in H_2S. Describe the precipitate that forms.

Repeat the experiment, diluting the mixture to 100 ml. instead of to 50 ml. What is the yellow precipitate? Write the equation. From these two experiments state the best conditions for the precipitation of CdS.

Action of Ammonium Polysulfide on CdS. Treat some of the precipitated CdS with $(NH_4)_2S_2$, warming the mixture. Does the sulfide dissolve? What other sulfides show a similar behavior?

Action of Dilute HNO_3 on CdS. Treat the remainder of the CdS with dilute HNO_3, warming if necessary. Show how the equation for the reaction is balanced. What other sulfides already studied show a like behavior toward HNO_3?

2. Complex Ion of Cadmium and Ammonia. Neutralize the nitric acid solution obtained in (1) with dilute NH_4OH and then enough of the reagent to dissolve any $Cd(OH)_2$ which may form.

In what form is the cadmium now? Write the equation. Compare this behavior with that for copper.

3. Complex Ion of Cadmium and Cyanide. Add, dropwise, KCN reagent to the solution containing $Cd(NH_3)_4^{++}$ until the precipitate which first forms redissolves. What forms first? In what form is the cadmium when an excess of CN^- has been added? Write the equations.

Pass H_2S into the solution. What is the yellow precipitate? Explain how KCN and H_2S can be used to identify cadmium in the presence of copper.

REVIEW EXERCISES — SET 11

1. Group together the equations showing the reactions of the cations of this subgroup with H_2S, specifying the color of each sulfide.

2. What effect, if any, has ammonium polysulfide on the sulfides of this subgroup?

3. What effect has dilute HNO_3 on the sulfides of this subgroup? Write the balanced molecular equations for the reactions which take place.

4. What property of the lead ion enables one to separate it from bismuth, copper and cadmium? Write the necessary equation.

5. Show, by equations, what difference in behavior toward excess NH_4OH is shown by bismuth, copper and cadmium which enables one to separate bismuth from copper and cadmium.

6. Show, by equations, how cupric ion differs from cadmium ion in the behavior toward excess KCN.

7. Write equations showing (*a*) an identifying property (test) for the mercuric ion, (*b*) two identifying tests for lead, (*c*) two identifying tests for bismuth, (*d*) two for copper, (*e*) a test for cadmium when originally present with copper.

8. In what group of the periodic table is each of these elements found? What valence or valences does each of these elements show? Assemble the equations, showing how certain of these cations are either oxidized or reduced, as revealed in the preliminary experiments.

9. Summarize the instances in which (*a*) hydrolysis, (*b*) complex-ion formation, (*c*) oxidation or reduction is a pronounced property of these cations.

10. Would the sulfides of this subgroup be more easily or more difficultly precipitated in a solution less acid than that employed in the individual experiments?

OUTLINE OF METHOD OF ANALYSIS OF THIS SUBGROUP

The members of Group II as a whole, including arsenic, antimony and tin which make up subdivision B, also called the tin subgroup, are precipitated as sulfides by the use of hydrogen

sulfide under carefully regulated conditions of acidity, dilution and temperature so that the sulfides of Group III are prevented from forming. The group precipitate is then subdivided by the use of ammonium polysulfide, in which reagent the sulfides of Division A are practically insoluble.

Careful study of the properties of the members of this subgroup, as revealed through the preliminary experiments and review exercises, lead further to the following conclusions:

1. In regard to the conditions under which the group precipitation is made, the necessity of a careful regulation of the acidity has already been emphasized. The student should not get the wrong impression that the sulfides of this group can be precipitated only from an acid solution. Quite the contrary is true, and if the precipitation is not complete here, the ions escaping precipitation in this group will nevertheless be precipitated in Group III where their presence will seriously interfere with the separation and detection of the members of the ammonium sulfide group. The same applies to silver and mercurous mercury, for if these ions are not completely removed in Group I, they will be precipitated as Ag_2S and Hg_2S in Group II.

To effect a separation of the sulfides of Group II from those of Group III the solution should be 0.3 *M* with respect to HCl. This is accomplished by the addition of 2.5 ml. of concentrated HCl to the solution, which finally is diluted to 100 ml. Instead of using the concentrated acid, 10 ml. of more dilute (3 *M*) HCl is sometimes used. The use of an indicator is advantageous to establish definitely the correct acidity of the solution. Methyl violet is sometimes recommended. Ware (Essentials of Qualitative Chemical Analysis) recommends acid cresol red, the color shade being close to the transition tint from pink to orange-yellow.

For the complete precipitation of arsenic, the solution should be relatively strongly acid and hot; on the other hand, cadmium, tin and lead are best precipitated from a cold, dilute solution. These conditions are taken care of in the detailed procedure which follows.

2. Of the sulfides of Division A, the only one which resists the action of dilute HNO_3 is HgS; hence this property is made use of in separating this sulfide from the others of this subgroup. HgS is soluble in aqua regia, and in this solution the presence of

DIAGRAMMATIC SCHEME — GROUP II

Solution: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++} (AsO_2^-), As^{+++++} ($AsO_4^{\equiv}$), Sb^{+++}, Sb^{+++++}, Sn^{++}, Sn^{++++}

Neutralized with NH_4OH; 2.5 ml. concentrated HCl added, dilute to 50 ml.; heated; H_2S passed in, diluted with 50 ml. cold water, H_2S passed in. Filtered.

- *Precipitate:* HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2

  Precipitate treated with 10 ml. $(NH_4)_2S_x$. Filtered.

  - *Residue:* HgS, PbS, Bi_2S_3, CuS, CdS

    Heated with 20 ml. dilute HNO_3. Filtered.

    - *Residue:* HgS — Dissolved in aqua regia, $SnCl_2$ added — gray or black residue proves Hg.
    - *Filtrate:* Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}

      5 ml. concentrated H_2SO_4 added evaporated to SO_3 fumes, poured into 20 ml. water. Filtered.

      - *Residue:* $PbSO_4$ — Dissolved in hot $NH_4C_2H_3O_2$; K_2CrO_4 added — yellow $PbCrO_4$ proves Pb.
      - *Filtrate:* Bi^{+++}, Cu^{++}, Cd^{++}

        A slight excess of NH_4OH added. Filtered.

        - *Residue:* $Bi(OH)_3$ — Dissolved in HCl, diluted—Na_2SnO_2 black proves Bi.
        - *Filtrate:* $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$ — Deep blue solution proves Cu — KCN added until colorless. (Careful! Violent Poison!) H_2S passed in — yellow CdS proves Cd.

  - *Filtrate:* $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^{=}$

    Acidified with dilute HCl.

    - *Precipitate:* As_2S_5, Sb_2S_5, SnS_2

      Treated with concentrated HCl. Warmed and filtered.

      - *Residue:* As_2S_5 — Dissolved in dilute HNO_3, filtered, magnesia mixture added — white $MgNH_4AsO_4$ proves As.
      - *Filtrate:* Sb^{+++}, Sn^{++++}

        Diluted to 50 ml., H_2S passed in. Filtered.

        - *Residue:* Sb_2S_3 — (Orange) — Dissolved in HCl, Al wire added, warmed — black deposit, insoluble in NaOCl proves Sb. Rhodamine-B test.
        - *Filtrate:* Sn^{++++} — Iron nail added, warmed, filtered into $HgCl_2$—white precipitate turning black proves Sn. Flame test.

mercuric ions can be shown by the reducing action of stannous chloride.

3. The action of dilute H_2SO_4 on test solutions of Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++} has shown that $PbSO_4$ only is precipitated, thus offering a means of separating lead from bismuth, copper and cadmium. $PbSO_4$ is soluble in $NH_4C_2H_3O_2$, from which solution the lead can be reprecipitated as $PbCrO_4$.

4. Ammonium hydroxide will precipitate $Bi(OH)_3$, insoluble in an excess of the reagent, whereas the hydroxides of copper and cadmium are soluble in NH_4OH, forming complex metal-ammonia ions. This reagent will therefore separate bismuth from copper and cadmium. Bismuth can be tested for by the formation of bismuth oxychloride, or by reduction to metallic bismuth with sodium stannite.

5. Copper and cadmium behave alike toward all the reagents introduced up to this point. In order to detect cadmium, when the deep blue color of the complex $Cu(NH_3)_4^{++}$ ion reveals the presence of copper, use is made of an excess of KCN, which reduces the cupric ion to the cuprous condition, forming a stable complex cuprocyanide ion, and thus lowers the concentration of the cuprous ion so that when H_2S is passed into the solution no Cu_2S will form. CdS, however, will be precipitated, serving as a test for cadmium.

In short, the procedure of separating each member from others of this subgroup consists in the successive use of dilute HNO_3, dilute H_2SO_4, NH_4OH and KCN. The elements, now isolated from each other, are in the form, respectively, of HgS, $PbSO_4$, $Bi(OH)_3$, $Cu(CN)_4^{-}$ and CdS. Identifying tests are then applied as already indicated.

A diagrammatic arrangement of the scheme of separation and identification, including Division B as well, appears on page 147. The detailed procedure for the analysis of a known mixture of Division A follows.

Practice Analysis of a Mixture Containing Mercuric Mercury, Lead, Bismuth, Copper and Cadmium Ions

In a 100-ml. measuring cylinder place 5 ml. of each of the test solutions of Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++}, neutralize with dilute NH_4OH, make faintly acid with dilute HCl and then add 2.5 ml. of concentrated HCl. Dilute the mixture to 50 ml. with

distilled water. Transfer the solution to an Erlenmeyer flask and pass in a rapid stream of hydrogen sulfide until precipitation appears to be complete.

The reactions involved in the precipitation of the sulfides of this subgroup are shown by the ionic equations:

$$Hg^{++} + S^{=} = \underline{HgS}$$

$$Pb^{++} + S^{=} = \underline{PbS}$$

$$2Bi^{+++} + 3S^{=} = \underline{Bi_2S_3}$$

$$Cu^{++} + S^{=} = \underline{CuS}$$

$$Cd^{++} + S^{=} = \underline{CdS}$$

Filter off the precipitate and test the filtrate with H_2S in order to be sure that precipitation is complete. Wash the precipitate on the filter with small portions of water, saturated with H_2S and containing a small quantity of NH_4NO_3.

Separation of HgS and Identification of Mercury. Transfer the precipitated and washed sulfides to a beaker, add 20 ml. of dilute HNO_3 (made by adding 7 volumes of water to 1 volume of concentrated HNO_3), heat for several minutes while stirring constantly and then filter.

The residue consists of HgS or possibly the double salt, $2HgS \cdot Hg(NO_3)_2$ and free sulfur; the filtrate contains Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++}, the sulfides of these ions having dissolved in the nitric acid.

To identify mercury in the black residue, wash it with water, transfer to a beaker with a spatula and boil with 5 ml. of aqua regia until brown fumes of NO_2 are no longer given off and all chlorine is evolved. Be careful not to allow the solution to evaporate to dryness. Dilute the solution with 5 ml. of water and filter. The filtrate contains the mercuric ion.

To this filtrate add, drop by drop, $SnCl_2$ reagent. This will reduce the Hg^{++} ion, first to the mercurous state, precipitating white Hg_2Cl_2 which, on further reduction, results in finely divided black metallic mercury. The precipitate, changing color from a white, through shades of gray to black, shows the presence of mercury

Separation of $PbSO_4$ and Identification of Lead. The filtrate from the separation of mercury will contain Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++} ions and excess HNO_3. Place the filtrate in an evaporating dish, add 5 ml. of concentrated H_2SO_4 and evaporate under the hood until white, cloudy fumes of SO_3 appear. This will not occur until all the HNO_3 has been evolved and the volume reduced to a few milliliters. It is important that all HNO_3 be removed because $PbSO_4$ is somewhat soluble in this acid and its presence in the filtrate will interfere with the test for bismuth.

Cool the solution and pour it slowly into 20 ml. of water, wash the dish with a few milliliters of water, adding this to the solution; allow the mixture to settle and then filter. Reserve this filtrate for the identification of the Bi^{+++}, Cu^{++} and Cd^{++} ions. The white, finely crystalline precipitate is a good indication of lead. Basic bismuth sulfate, $(BiO)_2SO_4$, may appear at this point, and may be mistaken for $PbSO_4$; hence the confirmatory chromate test for lead should be made.

Wash the white precipitate with a little water and then pour through the filter 10 ml. of hot $NH_4C_2H_3O_2$ solution. Reheat the filtrate and repeat the extraction. Add a few milliliters of acetic acid and several drops of K_2CrO_4 to the filtrate. The yellow precipitate of $PbCrO_4$ shows the presence of lead.

Separation of $Bi(OH)_3$ and Identification of Bismuth. Neutralize the filtrate from the lead separation with dilute NH_4OH, and then add a few milliliters in excess, in order to dissolve copper and cadmium hydroxides. The white precipitate remaining is $Bi(OH)_3$.

Filter off the white precipitate and wash it with water. Dissolve a portion in a few drops of dilute HCl and pour the solution into about 50 ml. of warm water. A white precipitate or turbidity is due to BiOCl.

The test for bismuth is carried out as follows: Prepare fresh sodium stannite, Na_2SnO_2, by adding NaOH to a few milliliters of $SnCl_2$ solution until the precipitate, which first forms, dissolves. Cool the reagent and add a few drops to the $Bi(OH)_3$ remaining on the filter paper. The residue will turn dark owing to the reduction of the bismuth to the free state.

Identification of Copper. The deep blue solution obtained during the $Bi(OH)_3$ separation, owing to complex copper-ammonia ions, $Cu(NH_3)_4^{++}$, is usually sufficient proof of the presence of copper (see note under arsenic test, page 302).

For traces of copper, the test with potassium ferrocyanide, $K_4Fe(CN)_6$, is more sensitive. To carry out this test, take a small portion of the solution, make it slightly acid with H_2SO_4 and add a few drops of dilute $K_4Fe(CN)_6$ solution. A reddish brown color due to $Cu_2Fe(CN)_6$ identifies copper. Care must be taken not to add an excess of the reagent, otherwise white $Cd_2Fe(CN)_6$ will form.

Identification of Cadmium. The only test by which cadmium can be recognized is the formation of yellow cadmium sulfide. Since under the present conditions copper is also present, the precipitation of black CuS obscures the color of CdS. Accordingly CuS is prevented from precipitating by the use of KCN. This reagent suppresses the concentration of the copper ion to such an extent that, when H_2S is added no black sulfide of copper can form.

In carrying out this test *use utmost care with KCN, since this reagent is a violent poison. Carry out the test under the hood.* Proceed as follows:

Add KCN to the deep blue solution until the color is discharged and the precipitate which first forms dissolves in the excess of reagent. Then saturate the solution with H_2S. Under these conditions copper does not precipitate but cadmium does as yellow CdS. If this sulfide precipitate is dark-colored, treat it with 3 ml. of 1:4 H_2SO_4, filter, dilute the filtrate to about 50 ml. and pass in H_2S. A yellow precipitate shows the presence of cadmium.

See the preliminary experiments with KCN for an explanation of the above test for cadmium in the presence of copper (page 143).

The Ions of Division B, Group II

ARSENIC, As^{+++} AND As^{+++++}

Arsenic forms two series of compounds: the arsenious, in which the element is trivalent, and the arsenic, in which the element is pentavalent. These compounds may be considered as being derived from the two oxides, As_2O_3 and As_2O_5. Moreover, these oxides are somewhat amphoteric and hence give rise to salts in which the element may be either in the cation or in the anion form. Thus the trivalent forms may be such compounds as $AsCl_3$ and H_3AsO_3 or $HAsO_2$ whereas the pentavalent forms are such compounds as $AsCl_5$ and H_3AsO_4.

The arsenious test solution supplied in the laboratory contains arsenic in its trivalent forms. It can be prepared by treating As_2O_3 with dilute HCl. Arsenic trioxide dissolves to a limited extent in water, according to the equation:

$$As_2O_3 + 3H_2O = 2H_3AsO_3$$

The product formed, here written as orthoarsenious acid, is an amphoteric substance and may also be assigned the formula $As(OH)_3$. As a tribasic acid, this substance ionizes in three stages, as shown by the equations:

$$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_3^-$$

$$H_2AsO_3^- \rightleftharpoons H^+ + HAsO_3^=$$

$$HAsO_3^= \rightleftharpoons H^+ + AsO_3^{\equiv}$$

giving rise to the three anions in decreasing concentrations.

Furthermore, by the loss of a molecule of water from the ortho form, meta-arsenious acid, $HAsO_2$, is formed:

$$H_3AsO_3 \rightarrow HAsO_2 + H_2O$$

Meta-arsenious acid is a weak monobasic acid which, by undergoing slight dissociation, produces the meta-arsenite ion:

$$HAsO_2 \rightleftharpoons H^+ + AsO_2^-$$

Although these four anion forms may exist in an arsenious solution, the undissociated $HAsO_2$ undoubtedly predominates. Moreover, acidification of an aqueous solution of the oxide increases the solubility of the oxide and promotes the formation of the cation in the form of ionized $AsCl_3$.

$$H_3AsO_3 + 3H^+ + 3Cl^- \rightleftharpoons As^{+++} + 3Cl^- + 3H_2O$$

Since this reaction is reversible, a solution of As_2O_3 dissolved in HCl contains the several anion forms as well as $HAsO_2$ and As^{+++}, the relative amounts depending on the concentration of the HCl present.

The test solution containing pentavalent arsenic may be made by dissolving arsenic pentoxide in water:

$$As_2O_5 + 3H_2O = 2H_3AsO_4$$

forming arsenic acid, which may, like H_3AsO_3, undergo ionization in three stages, thus:

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$$

$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^=$$

$$HAsO_4^= \rightleftharpoons H^+ + AsO_4^{\equiv}$$

Such a solution consists chiefly of the $H_2AsO_4^-$ ion but contains a certain, though small, concentration of $HAsO_4^=$ and a still smaller concentration of the orthoarsenate, $AsO_4^{\equiv}$, ion.

The reactions of arsenic with hydrogen sulfide are extremely important and the best conditions for the precipitation of the sulfides of arsenic must be clearly understood if trouble is to be avoided. If H_2S is passed into a solution containing arsenic in its trivalent forms, the solution being first acidified with HCl (2.5 ml. of concentrated HCl per 50 ml. of solution), an immediate and rapid precipitation of yellow arsenious sulfide, As_2S_3, results. Since the arsenic is present almost entirely in the form of $HAsO_2$ the reaction is best shown by the equation:

$$2HAsO_2 + 3H_2S = As_2S_3 + 4H_2O$$

If the arsenious solution is too weakly acid with HCl, the sulfide will not precipitate and coagulate; instead colloidal As_2S_3 will form and produce a yellow turbidity.

With solutions containing the arsenate (pentavalent) forms, the effect of H_2S is more varied, depending upon the conditions of acidity and temperature.

These conditions may be summarized as follows:

1. If hydrogen sulfide is passed into a cold solution of an arsenate containing a very large excess of concentrated hydrochloric acid, the arsenic is precipitated mainly as the yellow pentasulfide, As_2S_5:

$$H_3AsO_4 + 5H_2S = \underline{As_2S_5} + 8H_2O$$

2. If, under the same condition of high acidity, the solution is heated and H_2S is passed in, some of the arsenic is precipitated directly as As_2S_5 and some is first reduced by the H_2S to $HAsO_2$:

$$H_3AsO_4 + H_2S = HAsO_2 + S + 2H_2O$$

and then precipitated as As_2S_3:

$$2HAsO_2 + 3H_2S = \underline{As_2S_3} + 4H_2O$$

and there will result a mixture of As_2S_5, As_2S_3 and S.

3. If the acidity is only moderate (2.5 ml. of concentrated HCl per 50 ml. of solution) and the solution is cold, the arsenate is slowly reduced by the H_2S and only after a long time will there be formed a precipitate consisting of the trisulfide.

4. If a reducing agent such as ammonium iodide is added to a moderately acidified solution of an arsenate and then H_2S is passed into the solution, there will be a rapid precipitation of As_2S_3. The reduction of the arsenate solution by NH_4I may be shown by the equation:

$$H_3AsO_4 + 2I^- + 2H^+ = HAsO_2 + I_2 + 2H_2O$$

Arsenic pentasulfide is soluble in ammonium polysulfide sulfide, according to the equation:

$$\underline{As_2S_5} + 3S^= = 2AsS^{\equiv}_4$$

forming the complex thioarsenate ion, analogous to the $AsO_4^{\equiv}$ ion, in which sulfur has replaced oxygen in the anion.

Arsenic trisulfide likewise dissolves in this reagent, the arsenic being at the same oxidized, forming the thioarsenate ion, identical with that formed from the pentasulfide. The equation for this reaction may be derived on the basis of the following considerations. The oxidizing agent is probably the disulfide ion, $S_2^=$, present in the polysulfide reagent. This may be considered as being reduced to the monosulfide ion:

$$S_2^= + 2e = 2S^= \qquad (1)$$

The As_2S_3 is converted into the thioarsenate ion as indicated in the equation:

$$\underline{As_2S_3} + 5S^= = 2AsS_4^{\equiv} + 4e \qquad (2)$$

As a net result we have, multiplying equation (1) by 2 and adding the two equations:

$$\underline{As_2S_3} + S^= + 2S_2^= = 2AsS_4^{\equiv}$$

This equation, regarded from a molecular standpoint, would be written:

$$\underline{As_2S_3} + (NH_4)_2S + 2(NH_4)_2S_2 = 2(NH_4)_3AsS_4$$

When a solution of thioarsenite is acidified with dilute HCl, As_2S_3 precipitates. Likewise when a thioarsenate solution is acidified with dilute HCl, the pentasulfide precipitates and H_2S is evolved:

$$2AsS_4^{\equiv} + 6H^+ = \underline{As_2S_5} + \overline{3H_2S}$$

The sulfides of arsenic are also soluble in hot, concentrated HNO_3. In the case of As_2S_3 the arsenic is oxidized to the arsenate form and NO_2 is evolved, the sulfide ion being oxidized either to free sulfur or to $SO_4^=$.

In the case of As_2S_5, the products are $H_2AsO_4^-$, S, NO_2 and water. The balancing of the equation for the action of concentrated HNO_3 on As_2S_5 is accomplished as follows. The nitrate ion is the oxidizing agent and is reduced to NO_2, requiring one electron for each NO_3^- reduced:

$$NO_3^- + 2H^+ + 1e = NO_2 + H_2O \qquad (1)$$

The other half-cell reaction is the oxidation of the 5 sulfide ions to free sulfur:

$$5S^= = 5S^0 + 10e$$

and this, combined with the formation of $H_2AsO_4^-$, which requires 4 oxygen atoms for each atom of arsenic, results in the equation:

$$As_2S_5 + 8H_2O = 2H_2AsO_4^- + 12H^+ + 5S + 10e \qquad (2)$$

Obviously, to balance electrons, equation (1) must be multiplied by 10, and we have:

$$10NO_3^- + 20H^+ + 10e = 10NO_2 + 10H_2O$$

$$As_2S_5 + 8H_2O = 2H_2AsO_4^- + 12H^+ + 5S + 10e$$

$$\underline{As_2S_5} + 10NO_3^- + 8H^+ = \overline{10NO_2} + 2H_2O + 2H_2AsO_4^- + \underline{5S}$$

Arsenites are reducing agents and are oxidized by a number of oxidizing substances. The reaction with iodine is an important one since, as we shall see later in the study of anions, it is employed to distinguish or detect arsenites in the presence of arsenates. The reaction is:

$$AsO_2^- + 2H_2O + I_2 = H_2AsO_4^- + 2I^- + 2H^+$$

Arsenates act as oxidizing agents toward certain substances as, for example, H_2S, as already shown. The reaction toward the iodide ion:

$$H_2AsO_4^- + 2I^- + 2H^+ = AsO_2^- + 2H_2O + I_2$$

is, as will be observed, the reverse of the reaction of arsenites toward I_2. In fact, the two equations just given reveal an interesting reversible reaction. The latter equation represents the test for an arsenate in the presence of an arsenite, as conducted in the anion procedure.

For identifying tests for the arsenate ion, as applied in the cation procedure, there are three important reactions. These are:

1. Silver nitrate, in a neutral solution will precipitate chocolate-colored silver arsenate:

$$3Ag^+ + AsO_4^{\equiv} = \underline{Ag_3AsO_4}$$

2. Magnesia mixture (a mixture of $MgCl_2$ and NH_4OH, buffered by NH_4Cl) forms a white, crystalline precipitate of magnesium ammonium arsenate:

$$Mg^{++} + NH_4^+ + AsO_4^{\equiv} = \underline{MgNH_4AsO_4}$$

3. Ammonium molybdate, in a warm, nitric acid solution, reacts to form a bright yellow, finely divided precipitate known as ammonium arsenomolybdate:

$$AsO_4^{\equiv} + 12MoO_4^{=} + 3NH_4^+ + 24H^+ =$$
$$\underline{(NH_4)_3AsO_4 \cdot 12MoO_3} + 12H_2O$$

In molecular form this equation is written:

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 =$$
$$(NH_4)_3AsO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

Reactions analogous to (2) and (3) take place with the phosphate ion but not with the arsenite ion.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of As_2S_3 and As_2S_5. (*a*) To 5 ml. of arsenite test solution add 2.5 ml. of concentrated HCl, dilute to 50 ml. and pass in H_2S. Note the color of the sulfide formed and write the equation. Reserve the precipitate for further experiments.

(*b*) Repeat the experiment using the arsenate test solution. Is there an immediate precipitate formed? Heat the solution and again pass in H_2S. What is formed?

(*c*) Dilute 5 ml. of arsenate test solution to 45 ml. with water, add 2 ml. of ammonium iodide reagent and acidify with 2.5 ml. of concentrated HCl. Show what happens by writing the equation. Then pass H_2S into this reduced solution. What forms? Give the equation.

Action of Ammonium Polysulfide on As_2S_3. Filter off the As_2S_3 obtained in (*a*) above, transfer it to a small dish and treat it with a few milliliters of $(NH_4)_2S_2$, stirring until solution takes place. In what form is the arsenite now? Give the equation.

Acidify the solution containing the thioarsenate with dilute HCl. What is the precipitate which forms?

As_2S_5 is insoluble in concentrated HCl. Dissolve it by treating with concentrated HNO_3. Show how the equation is balanced.

2. Tests for the Arsenate Ion. Perform the following experiments, which reveal the properties upon which identifying tests for arsenic are based.

(*a*) To the solution obtained by dissolving As_2S_5 in nitric acid, add NH_4OH until the solution is neutralized as shown by litmus paper, and then add some silver nitrate reagent. What color is silver arsenate? Write the equation.

(*b*) To a solution of an arsenate, add an equal volume of magnesia mixture. If precipitation does not result at once, shake the tube vigorously and set aside for further observation. Describe the precipitate and give the equation for its formation.

(*c*) Add dilute HNO_3 to a few milliliters of arsenate test solution, add ammonium molybdate and warm but do not boil. What is the finely divided yellow precipitate? This is an important reaction and the balancing of the equation should be mastered.

ANTIMONY, Sb^{+++} AND Sb^{+++++}

Antimony, like arsenic, forms two series of compounds, the trivalent or antimonious, and the pentavalent or antimonic. The two important oxides, Sb_2O_3 and Sb_2O_5, are amphoteric and both yield, like the corresponding oxides of arsenic, two types of compounds in which the element may exist in either cation or anion

form as, for example, $SbCl_3$ and H_3SbO_3, representing trivalent forms, and $SbCl_5$ and H_3SbO_4, typical of the pentavalent types. Antimony salts are easily hydrolyzed like those of bismuth and tin; they yield insoluble compounds.

Among the trivalent forms, $SbCl_3$ and Sb_2S_3, are the most important salts from an analytical standpoint. $SbCl_3$, when treated with water, readily hydrolyzes to SbOCl:

$$SbCl_3 + HOH = \underline{SbOCl} + 2Cl^- + 2H^+$$

SbOCl is antimonyl chloride, sometimes called antimony oxychloride, and contains the antimonyl, SbO, group. The test solution containing the trivalent ion is made by adding sufficient HCl to $SbCl_3$ to prevent hydrolysis to SbOCl. The antimonyl ion unites with a number of organic anions to form stable organic complexes; for example, with the tartrate ion, $(SbO)C_4H_4O_6^-$ ions are formed, in this way preventing the precipitation of antimony compounds. In a solution of $SbCl_3$ containing a large amount of concentrated HCl, the antimony probably exists as $SbCl_6^{\equiv}$, the chloroantimonite ion.

The important pentavalent compounds are $SbCl_5$, Sb_2S_5 and orthoantimonic acid, H_3SbO_4. The latter results when $SbCl_5$ completely hydrolyzes:

$$SbCl_5 + 4HOH = \underline{H_3SbO_4} + 5H^+ + 5Cl^-$$

Both Sb_2S_3 and Sb_2S_5 are orange-red in color and are readily precipitated when H_2S is passed into solutions of $SbCl_3$ and $SbCl_5$, respectively, provided these solutions are not too strongly acidified.

Both sulfides dissolve in ammonium polysulfide to form the thioantimonate ion. In the case of Sb_2S_5, the complex thio-ion forms directly:

$$Sb_2S_5 + 3S^= = 2SbS_4^{\equiv}$$

In the case of Sb_2S_3, however, the antimony is oxidized to the pentavalent state, forming the thioantimonate ion. As with arsenic trisulfide, the oxidizing agent is probably the disulfide ion, $S_2^=$, this half-cell reaction doubtless being:

$$S_2^= + 2e = 2S^=$$

The oxidation of Sb_2S_3 and conversion into $SbS_4^{\equiv}$ may be rep-

resented by the equation

$$\underline{Sb_2S_3} + 5S^{=} = 2SbS_4^{\equiv} + 4e$$

giving

$$Sb_2S_3 + 2S_2^{=} + S^{=} = 2SbS_4^{\equiv}$$

Acidification of a thioantimonate solution results in the precipitation of Sb_2S_5:

$$2SbS_4^{\equiv} + 6H^+ = Sb_2S_5 + 3H_2S$$

Both sulfides are soluble in concentrated HCl, forming Sb^{+++}. In the case of the pentasulfide, the dissolving is accompanied by reduction of the Sb^{+++++} to Sb^{+++} and liberation of sulfur:

$$Sb_2S_5 + 6H^+ = 2Sb^{+++} + 3H_2S + \underline{2S}$$

Antimonic salts are reduced by iodides such as NH_4I to the trivalent state; the iodide ion is oxidized to I_2.

Metals standing above antimony in the electromotive series will reduce the ions of antimony to the metallic condition. With aluminum, the Sb forms a black, spongy deposit. This redox reaction is resolved into:

$$
\begin{array}{rcl}
Al^0 & = & Al^{+++} + 3e \\
Sb^{+++} + 3e & = & Sb^0 \\
\hline
Al^0 + Sb^{+++} & = & Al^{+++} + Sb^0
\end{array}
$$

By using a Zn–Pt couple, the deposited Sb appears as a black stain on the surface of the bright platinum. The stain is insoluble in sodium hypochlorite. The reduction of antimony to the metallic state is a common test for this element. A further, confirmatory test is that carried out by the dyestuff, rhodamine-B. This test is described below.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of Sb_2S_3 and Sb_2S_5. (*a*) To 5 ml. of $SbCl_3$ test solution, add 2.5 ml. of concentrated HCl, dilute to 50 ml. and pass in H_2S. Note the color of the sulfide formed and write the equation. Reserve the precipitate for further experiments.

(*b*) Repeat the experiment using a solution of $SbCl_5$. What forms? Write the equation.

Action of Ammonium Polysulfide on Sb_2S_3. Filter off the Sb_2S_3 obtained in 1(*a*), transfer it to a small dish and add some $(NH_4)_2S_2$, warming if necessary to dissolve the precipitate. What has formed? Compare the result with that obtained with As_2S_3. Record the equation for the reaction.

Add concentrated HCl to the solution just obtained. In what form is the antimony now? Account for the formation of sulfur. Show how this redox reaction is balanced.

2. Separation of Antimony from Tin. Take 5 ml. of $SbCl_3$ test solution, add 10 ml. of concentrated HCl, dilute to 50 ml. and heat almost to boiling. While hot pass in H_2S for 5 minutes. Sb_2S_3 precipitates, but under the same conditions tin sulfide will not precipitate. This constitutes a method for the separation of antimony from tin.

3. Reduction of Antimony. To 2 ml. of $SbCl_3$ test solution add a few pieces metallic aluminum in the form of chips, turnings or wire. Warm if necessary to start the reaction. What is the black spongy deposit? Explain the action of Al.

4. Rhodamine-B Test. The dyestuff, tetraethyl rhodamine, better known as rhodamine-B, forms a violet color with pentavalent antimony. To conduct this test the trivalent antimony solution must first be oxidized. Proceed as follows: Place not more than 1 ml. of test solution in a test tube, add some crystals of KNO_2 and several drops of concentrated HCl. After effervescence has ceased, add several drops of the dye reagent. A distinct color change from bright red to violet will be observed.

TIN, Sn^{++} AND Sn^{++++}

The element tin exists in two states of oxidation: one, the stannous, in which tin is divalent and the other, the stannic, in which tin is tetravalent. The compounds of tin may be considered as derived from SnO and SnO_2, respectively. These oxides are amphoteric and hence yield salts in which the tin may be present either as cation or anion just as in the case of antimony and arsenic. The commonest salts are stannous chloride, $SnCl_2$ and stannic chloride, $SnCl_4$. Like antimony and bismuth, the salts of tin are readily hydrolyzed, precipitating insoluble com-

pounds. The chlorides for example react in the following way:

$$Sn^{++} + 2Cl^- + HOH = Sn(OH)Cl + H^+ + Cl^-$$

$$Sn^{++++} + 4Cl^- + 4HOH = Sn(OH)_4 + 4H^+ + 4Cl^-$$

It is to prevent hydrolysis that the test solutions used in the laboratory are acidified with HCl.

In a solution of $SnCl_2$ containing a large amount of concentrated HCl, the tin probably exists as the chlorostannite, $SnCl_4^=$, ion rather than as Sn^{++}; likewise, in a solution of $SnCl_4$ containing considerable HCl, there is probably present the chlorostannate ion, $SnCl_6^=$.

Stannous hydroxide, $Sn(OH)_2$, precipitates when NaOH or NH_4OH is added to a $SnCl_2$ solution. The hydroxide is soluble in an excess of strong base forming the stannite ion:

$$Sn(OH)_2 + 2OH^- = SnO_2^= + 2H_2O$$

The stannate ion, $SnO_3^=$, forms in the same way, when a stannic solution is treated with an excess of NaOH. It is also formed when the stannite ion is oxidized, as in the test for bismuth.

From solutions containing stannous tin, H_2S will precipitate brown stannous sulfide:

$$Sn^{++} + S^= = \underline{SnS}$$

Stannic sulfide is yellow and is formed when a stannic solution is treated with H_2S:

$$Sn^{++++} + 2S^= = \underline{SnS_2}$$

Both SnS and SnS_2 dissolve in ammonium polysulfide to form the thiostannate ion. With SnS_2 the reagent forms directly the complex ion:

$$\underline{SnS_2} + S^= = SnS_3^=$$

With SnS, however, the Sn is oxidized to the stannic state with the formation of the thiostannate ion. The reaction is similar to those taking place with As_2S_3 and Sb_2S_3 and may be written thus:

$$\underline{SnS} + S_2^= = SnS_3^=$$

When a solution containing $SnS_3^{=}$ is acidified with dilute HCl, stannic sulfide is precipitated

$$SnS_3^{=} + 2H^+ = \underline{SnS_2} + \overline{H_2S}$$

A similar behavior is shown, it will be recalled, by the thioarsenate and the thioantimonate ions.

Stannic sulfide is also soluble in concentrated HCl:

$$\underline{SnS_2} + 4H^+ + 4Cl^- = Sn^{++++} + 4Cl^- + 2H_2S$$

Comparing the action of concentrated HCl here with its action on Sb_2S_5 it will be remembered that, in the latter, the dissolving of the pentasulfide is accompanied by a reduction of the antimony to Sb^{+++}. Further, As_2S_5 is not attacked by concentrated HCl. These differences are of importance in the scheme of separation.

The readiness with which the ions of tin are oxidized and reduced are important properties of this element.

Stannous solutions are strong reducing agents; in this connection the test for bismuth which uses a solution of sodium stannite should be recalled; in this test Bi^{+++} is reduced to the metallic form and the stannite ion becomes oxidized to the stannate form.

Metals which stand above tin in the electromotive series will either displace tin from its solutions or else reduce Sn^{++++} to Sn^{++}. Metallic zinc, for example, if placed in a stannous chloride solution, will reduce the ion to metallic tin. This redox reaction may be written thus:

$$\begin{array}{rcl} Sn^{++} + 2e & = & Sn^0 \\ Zn^0 & = & Zn^{++} + 2e \\ \hline Sn^{++} + Zn^0 & = & Sn + Zn^{++} \end{array}$$

This reaction is sometimes employed as a test for tin.

Metallic iron, such as an iron nail, will reduce the stannic to the stannous form; the equation is balanced by the half-cell reactions:

$$\begin{array}{rcl} Fe^0 & = & Fe^{++} + 2e \\ Sn^{++++} + 2e & = & Sn^{++} \\ \hline Sn^{++++} + Fe^0 & = & Sn^{++} + Fe^{++} \end{array}$$

Mercuric chloride is reduced by $SnCl_2$, first to Hg_2Cl_2, which is then reduced to Hg. This constitutes one of the tests for tin; it will be recalled that, conversely, this reaction is the test for mercury. The reaction has already been discussed under " Mercury," page 123.

PRELIMINARY EXPERIMENTS

1. Precipitation and Properties of SnS and SnS_2. Place 5 ml. of $SnCl_2$ test solution in a beaker, dilute to 100 ml. and pass in H_2S. Note the color of the precipitate. Write the equation. While the precipitate is being filtered, repeat the experiment with 5 ml. of $SnCl_4$ test solution. Note the color of the precipitate, write the equation and filter off the SnS_2.

Action of Ammonium Polysulfide on the Sulfides of Tin. Treat the SnS and SnS_2 with $(NH_4)_2S_2$. In what form is the tin in the filtrate from the SnS? Write the equation. Likewise, write the equation for the action of $(NH_4)_2S_2$ on SnS_2.

Combine the two filtrates containing the thiostannate ions and acidify with *dilute* HCl. What is the yellow precipitate which forms? Give the equation.

Action of Concentrated HCl on SnS_2. Filter off the precipitate obtained in the above experiment, wash thoroughly and then treat it with concentrated HCl. Compare the action here with the corresponding experiments with As_2S_5 and Sb_2S_5.

2. Reduction of Tin Salts. To 2 ml. of $SnCl_4$ solution, acidified with HCl, add an iron nail. To what is the ion reduced and the iron oxidized? Show this by a redox equation.

3. Mercuric Chloride Test for Tin. To the stannous chloride solution obtained in experiment 2 add $HgCl_2$ reagent. Note how the color of the precipitate changes as the reagent is gradually added. Give the equations.

4. Flame Coloration Test. Place about 1 ml. of stannous chloride solution in a small dish; add a small quantity of dilute HCl and a piece of zinc. Place some cold water in a crucible and, after action of the acid with the test solution has proceeded for some time, pick up the crucible with a pair of tongs, immerse it in the test solution and then hold it in the practically colorless flame of a burner. Where the flame impinges upon the lower part of the crucible, there will be observed an intense, blue-colored flame.

REVIEW EXERCISES — SET 12

1. Give formulas for the several ions derived from (*a*) trivalent and pentavalent arsenic; (*b*) trivalent and pentavalent antimony and (*c*) stannous and stannic tin.

2. Assemble the equations for the reactions which take place during the precipitation of the sulfides of arsenic, antimony and tin when test solutions are treated with H_2S.

3. Write the equations showing how As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS and SnS_2 dissolve in $(NH_4)_2S_2$.

4. Show the result of acidifying solutions containing $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$ with dilute HCl, by writing the corresponding equations.

5. Compare the behavior of As_2S_5, Sb_2S_5 and SnS_2 toward concentrated HCl by giving the proper equations for the reactions. How, then, would you separate arsenic from antimony and tin?

6. What are three tests for arsenic? Give the equations for the reactions, together with the color and nature of the products formed with the test reagents.

7. What difference in property of the metal may serve to separate antimony from tin? Explain the action involved.

8. Describe two tests for antimony and two for tin.

9. Under what conditions is arsenic best precipitated as a sulfide? Tin? Cadmium?

10. Carefully review the preliminary experiments and assemble, in the form of equations, the instances in which each element is either oxidized or reduced.

Outline of Method of Analysis of this Subgroup

Summarizing the properties of arsenic, antimony and tin as revealed in the preliminary experiments and review exercises it appears that:

1. By due care in regulating the acidity, volume of solution and temperature, the sulfides of arsenic, antimony and tin are precipitated by H_2S.

2. These sulfides dissolve in ammonium polysulfide to form the complex thio-ions, namely $AsS_4^{\equiv}$, $SbS_4^{\equiv}$ and $SnS_3^{=}$.

3. Acidification of the solutions containing these ions with dilute HCl results in the reprecipitation of As_2S_5, Sb_2S_5 and SnS_2.

4. By the action of concentrated HCl, Sb_2S_5 and SnS_2 are dissolved but As_2S_5 is not; this furnishes the means of separating arsenic from antimony and tin.

5. As_2S_5 may be dissolved in concentrated HNO_3 and the arsenate ion thus formed may be identified by the use of either $AgNO_3$, magnesia mixture or ammonium molybdate.

6. Antimony may be separated, if desired, from tin by a careful control of the sulfide-ion concentration, under conditions in which Sb_2S_3 may precipitate and the sulfides of tin may not.

7. Identifying tests for antimony and tin are described in the preceding experiments.

Practice Analysis of a Mixture Containing Arsenic, Antimony and Tin Ions

The separation and detection of arsenic, antimony and tin present more experimental difficulties than the other cations. The conditions of precipitation, subdivision and final identification must be precisely regulated, and more than usual care and experience are necessary for successful results. For these reasons, in the procedure for the analysis of a known mixture which follows, the conditions encountered in the analysis of unknown samples are adhered to as closely as possible.

Group Precipitation. Prepare a mixture containing arsenic, antimonous and stannic ions by taking 5 ml. of each of these test solutions. Neutralize the solution with dilute NH_4OH, add exactly 2.5 ml. of concentrated HCl, add NH_4I, transfer to a measuring cylinder and dilute to 50 ml. Heat the solution almost to boiling and pass in H_2S for 5 minutes. Then cool and dilute to 100 ml. and again pass in H_2S.

The purpose of the ammonium iodide is to reduce the arsenic to the arsenious condition, in which condition the precipitation with H_2S is more rapid.

The precipitation reactions are:

$$2HAsO_2 + 3H_2S = \underline{As_2S_3} + 4H_2O$$

$$2Sb^{+++} + 3S^{=} = \underline{Sb_2S_3}$$

$$Sn^{++++} + 2S^{=} = \underline{SnS_2}$$

Filter off the precipitate, washing twice with a few milliliters of water. Discard the filtrate and washings. Transfer the precipitate to a small beaker, add 10 ml. of ammonium polysulfide, warm and stir. When the precipitate has dissolved, add 10 ml. of water and filter off the residue of sulfur.

In order to reprecipitate the sulfides, so that their further separation can be effected, add enough dilute HCl to neutralize the solu-

serve the intense bluish color of the flame along the margin of the unglazed bottom of the crucible.

APPLICATION OF THEORY TO THE ANALYSIS OF THIS GROUP

In this, more than in any other cation or anion group, there are abundant examples of practically every fundamental principle and phenomenon involved in qualitative analysis. Outstanding among these is the classic example of common-ion effect, encountered in the precipitation of sulfides. Phenomena of complex-ion formation, amphoterism, hydrolysis, oxidation and reduction are abundantly illustrated. These are discussed in detail below.

Theory of the Sulfide Precipitation. If H_2S is passed into neutral solutions containing ions such as Hg^{++}, Cu^{++}, Mn^{++}, Fe^{++}, Zn^{++}, the corresponding sulfides will be formed; some of the sulfides, it is true, will precipitate more rapidly than others, but eventually all will be precipitated. If, however, the solutions are first acidified with HCl in the proportions of 2.5 ml. of concentrated HCl per 100 ml. of solution, and then H_2S is passed in, only the sulfides of Group II will be precipitated. These facts form the basis for the separation of Group II from Group III.

To explain the action of H_2S as a precipitating agent under these conditions, the following three points must be considered:

1. The ionization of H_2S.
2. The solubility product constants of the sulfides of these two groups.
3. The effect of a common ion on the H_2S equilibrium.

1. *The Ionization of H_2S.* Hydrogen sulfide is a weakly ionized, dibasic acid. It dissolves to some extent in water, forming at room temperatures a solution which is about 0.1 *M*. It ionizes in two stages, forming first H^+ ions and hydrosulfide, HS^-, ions:

$$\underset{\text{(dissolved)}}{H_2S} \rightleftharpoons H^+ + HS^- \text{ (primary ionization)}$$

The hydrosulfide ions further ionize to a slight extent into sulfide ions and hydrogen ions, according to the reaction:

$$HS^- \rightleftharpoons H^+ + S^= \text{ (secondary ionization)}$$

The primary and secondary ionization constants of H_2S and the concentrations of hydrogen ion, hydrosulfide ion and sulfide ion

which can exist in equilibrium with dissolved non-ionized H_2S have been determined by experiment. It has been found that in a liter of saturated solution of H_2S dissolved in water at 25° C. the concentrations are respectively 0.95×10^{-4} gram-ion of hydrogen ion, 0.95×10^{-4} gram-ion of hydrosulfide ion, 1.2×10^{-15} gram-ion of sulfide ions and 0.1 gram-mole of H_2S. If we combine the equilibrium expressions for the primary and secondary ionization of H_2S, namely:

$$\frac{C_{H^+} \times C_{HS^-}}{C_{H_2S}} = K_1 \text{ (primary) and } \frac{C_{H^+} \times C_{S^=}}{C_{HS^-}} = K_2 \text{ (secondary)}$$

we obtain the expression:

$$\frac{(C_{H^+})^2 \times C_{S^=}}{C_{H_2S}} = K_3 \text{ (ionization constant of } H_2S) = 1.1 \times 10^{-22}$$

Since, however, we are mainly interested in the amount of sulfide ion which is available for the precipitation of sulfides, and in the amount of H^+ ion which can be regulated at will, it is more convenient to rewrite the above expression in the form of the product of the ions by transposing the factor C_{H_2S}, which is practically constant (0.1 gram-mole). The product of the square of the hydrogen-ion concentration and the sulfide-ion concentration becomes:

$$(C_{H^+})^2 \times C_{S^=} = 1.1 \times 10^{-22} \times 0.1 = 1.1 \times 10^{-23}$$

In a liter of saturated H_2S the value of H^+ is, as already stated, 0.95×10^{-4}, and for $S^=$ it is 1.2×10^{-15}. Inasmuch as the above product represents an equilibrium condition, the value of 1.1×10^{-23} will always be maintained, though the concentration of H^+ or $S^=$ may be varied at will. If the H^+ ion concentration is greatly increased by the addition of a strong acid like HCl, the $S^=$ ions in equilibrium must greatly decrease; or, if the H^+ ions are practically removed by the addition of a base like NH_4OH, the $S^=$ ion concentration becomes enormous.

2. *Solubility Product Constants of Sulfides.* In order for a precipitate of any sulfide to form, the product of the ion concentration of the cation and that of the sulfide ion must exceed the value of the $K_{s.p.}$ of the sulfide in question. The solubilities in grams and in moles per liter and the solubility product constants for a number of sulfides are given in Table XI.

TABLE XI

Sulfide	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product Constant ($K_{s.p.}$)
HgS	1.5×10^{-24}	6.4×10^{-27}	4.1×10^{-53}
CuS	8.8×10^{-21}	9.2×10^{-23}	8.5×10^{-45}
CdS	8.6×10^{-13}	6.0×10^{-15}	3.6×10^{-29}
PbS	4.9×10^{-12}	2.0×10^{-14}	4.0×10^{-28}
ZnS	3.3×10^{-10}	3.4×10^{-12}	1.2×10^{-23}
FeS	3.4×10^{-8}	3.9×10^{-10}	1.5×10^{-19}
MnS	3.3×10^{-6}	3.8×10^{-8}	1.4×10^{-15}

These data have been collected from various sources. Data for the other insoluble sulfides of the metals either have not been determined or else are unreliable. Data for CoS and NiS are frequently given in solubility product tables, but the values are for allotropic forms of these sulfides and are not comparable to the values for other sulfides given in Table XI.

Recalling the fact that the constants represent solutions saturated with respect to the metallic and sulfide ions and using such concentrations of metallic ions as are employed in the test solutions, a sufficient sulfide-ion concentration from the ionization of H_2S can be maintained to exceed the value for the respective solubility product constants. The extremely small values for the constants for HgS and CuS, for instance, are quickly reached and exceeded; whereas, by using test solutions of the same strength for, say, zinc and manganese, relatively much greater concentrations of sulfide ion are required for saturation and subsequent precipitation of ZnS and MnS. It is convenient for the analyst to make a separation of the sulfides into two main groups (Group II and Group III). This is done by regulating the amount of $S^{=}$ ion available for precipitation, and is accomplished by the common-ion effect.

3. *The Effect of the Common Hydrogen Ions on the H_2S Equilibrium.* The condition to be adjusted to bring about a division of the sulfides into two groups is to limit the amount of $S^{=}$ ion which can exist in equilibrium with non-ionized H_2S, and this in turn is brought about by increasing the H^+ ion concentration through the addition of HCl. The order in which the sulfides are precipitated by successively decreasing the amount of HCl added (decreasing the amount of common ion) is: As_2S_3, HgS, CuS, Sb_2S_3, Bi_2S_3, SnS_2, CdS, PbS, SnS, ZnS, CoS, NiS, FeS, MnS.

For practical analytical purposes it is best to precipitate the sulfides of arsenic, antimony and tin, mercuric mercury, copper, bismuth, cadmium and lead and treat these as Group II. The cations of zinc, iron, nickel, cobalt, manganese, together with aluminum and chromium, are then left in solution to be later precipitated under conditions of high $S^{=}$ ion concentration and treated as Group III. The proper condition of acidity (H^+ ion concentration) to effect the precipitation of Group II sulfides and at the same time to prevent the precipitation of Group III sulfides, is attained by adding 2.5 ml. of concentrated HCl to the solution, which is finally diluted to 100 ml. This corresponds to about a 0.3 *M* solution. Neglecting the small concentration of H^+ ion already associated with H_2S, the new H^+ concentration is 0.3. The new $S^{=}$ concentration can be calculated as follows:

$$(0.3)^2 \times C_{S^=} = 1.1 \times 10^{-23}$$

Therefore,
$$C_{S^=} = 1.2 \times 10^{-22}$$

This extremely small concentration of ionic sulfur is still sufficient to cause precipitation of the metallic ions included in Group II.

Summarizing, the theory of the sulfide precipitation can be stated thus: By the repression of the sulfide ions through the addition of common H^+ ions the solubility-product constants are exceeded only in case of the cations of Group II.

Complex-Ion Formation. The formation of complex ions is also of considerable importance in the procedure of analysis. The behavior of arsenic, antimony and tin to form the complex metal-thio ions, namely, $AsS_4^{\equiv}$, $SbS_4^{\equiv}$ and $SnS_3^{=}$, through the action of $(NH_4)_2S_2$ on the sulfides of this subgroup is utilized to separate this subgroup from Division A. These complex thio ions are relatively unstable.

The method of separation of bismuth from copper and cadmium depends upon the formation of the cupric ammonia and cadmium ammonia complex ions. Moreover, the deep blue color of $Cu(NH_3)_4^{++}$ is a strong indication of the presence of copper. Finally, recourse is had to the relatively greater stability of the cuprous cyanide complex ion as compared to the cadmium cyanide complex ion in detecting cadmium in the presence of copper.

As already noted in the preliminary experiments, certain salts of mercury, bismuth, antimony and tin are subject to hydrolysis,

with the formation of insoluble basic salts. In fact, the hydrolysis of $BiCl_3$ to yield BiOCl constitutes a test for bismuth, and the presence of bismuth and antimony in the solution prepared for the analysis of Group I is usually revealed by the oxychlorides or oxynitrates of these elements.

Mention may also be made of the amphoteric nature, particularly of arsenic, antimony and tin as these elements undergo a series of changes involving cation and anion forms during their precipitation separation and identification.

Redox Reactions. These reactions are of very frequent occurrence. This is to be expected, inasmuch as all the elements of this group with the exception of cadmium have more than one valence, and all with the exception of cadmium and lead undergo oxidations or reductions in the process of analysis. The ions of these elements, therefore, in the oxidized state (higher valence) may act as oxidizing agents, and the lower-form ions may act as reducing agents. Among the reagents employed may be mentioned the oxidizing solvents, namely, nitric acid, aqua regia and ammonium polysulfide; the precipitating reagent, H_2S, which exerts a reducing effect; concentrated HCl, which acts as a reducing solvent on Sb_2S_5, and KCN, which, though used as a complex-ion forming reagent, reduces the copper to the cuprous state. In addition to these reagents, whose primary function is not oxidation or reduction, stannous chloride, sodium stannite and certain metals are employed as reducing agents.

THE AMMONIUM SULFIDE GROUP—GROUP III

NICKEL, Ni^{++}
COBALT, Co^{++}
MANGANESE, Mn^{++}
IRON, Fe^{++} and Fe^{+++}
ALUMINUM, Al^{+++}
CHROMIUM, Cr^{+++}
ZINC, Zn^{++}

The cations of this group are those that are precipitated by H_2S from an ammoniacal solution containing ammonium chloride. The precipitating agent is ammonium sulfide, $(NH_4)_2S$, formed by neutralization of the H_2S by the NH_4OH. The precipitating ion is the $S^{=}$ ion resulting from the ionization of $(NH_4)_2S$. The cations included here are: Ni^{++}, Co^{++}, Mn^{++}, Fe^{++} and Fe^{+++}, Zn^{++}, Al^{+++} and Cr^{+++}. The group reagent will precipitate NiS, CoS, MnS, FeS, Fe_2S_3, ZnS, together with $Al(OH)_3$ and $Cr(OH)_3$. The

sulfides of this group are formed only under conditions of rather high sulfide-ion concentration, since their solubility product constants are large compared with those of Group II. Hydrolysis takes place in the cases of aluminum and chromium, precipitating the hydroxides instead of the sulfides of these two metals.

The first separation of the group precipitate is made by the action of 1:9 HCl, in which NiS and CoS are practically insoluble, whereas the other sulfides and hydroxides dissolve readily. The filtrate from this separation is treated with NaOH and Na_2O_2, which results in the precipitation of iron as $Fe(OH)_3$ and of manganese as basic oxide $MnO(OH)_2$, leaving in the solution aluminum, chromium and zinc in the form of aluminate, AlO_2^-, chromate, $CrO_4^{=}$, and zincate, $ZnO_2^{=}$, ions, which are then further separated and identified as detailed later.

NICKEL, Ni^{++}

Nickel forms two series of salts, the nickelous, in which the valence of nickel is +2, and the nickelic in which the valence of the element is +3. The divalent compounds are better known and much more stable than the trivalent forms. Nickelous salts and the Ni^{++} ion are green. Nickelous hydroxide, $Ni(OH)_2$, is light green and is converted by strong oxidizing agents into black nickelic hydroxide, $Ni(OH)_3$. The hydroxides are formed when an alkali hydroxide, either NaOH or KOH, is added to a solution containing the nickelous or nickelic ion.

Ammonia solution when added in equivalent amount to a $Ni(NO_3)_2$ solution produces a greenish precipitate of the basic salt:

$$Ni^{++} + NO_3^- + OH^- = \underline{Ni(OH)NO_3}$$

An excess of the reagent will dissolve the precipitate forming a complex ion:

$$\underline{Ni(OH)NO_3} + 4NH_3 = Ni(NH_3)_4^{++} + OH^- + NO_3^-$$

The complex tetrammono-nickel ion will form directly if the ammonia reagent contains a considerable quantity of ammonium salt such as NH_4Cl. Here we have an example of common-ion effect, the high concentration of NH_4^+ so depressing the OH^- ion concentration that no precipitate can form.

Nickelous sulfide, NiS, is best precipitated by H_2S from solutions of nickelous salts which are made alkaline with ammonia. NiS is black; it has a tendency to form a brown, colloidal solution. The most favorable condition for the precipitation of NiS is from an ammoniacal solution containing NH_4Cl, for which the reaction can be written:

$$Ni(NH_3)_4^{++} + S^{=} = \underline{NiS} + 4NH_3$$

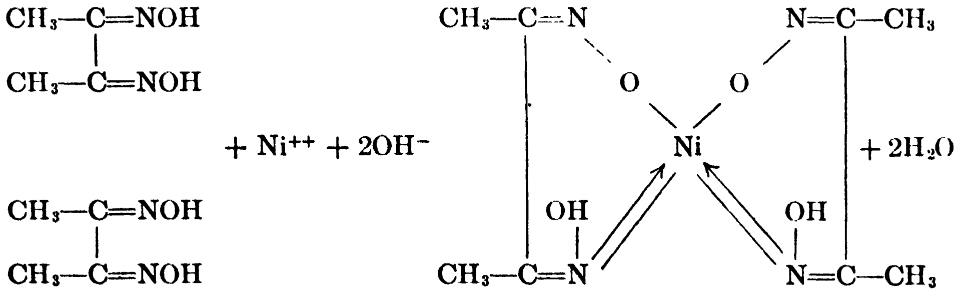
NiS is so slowly attacked by dilute HCl that it (as well as CoS) is not dissolved to any appreciable extent by this solvent; this fact furnishes the means of separating NiS (and CoS) from the other members of this group. It is, however, soluble in boiling concentrated HNO_3 and in aqua regia, with which it forms NO_2 and free sulfur. The reaction is written as follows:

$$\begin{aligned} 2(NO_3^- + 2H^+ + 1e &= NO_2 + H_2O) \\ NiS &= Ni^{++} + \underline{S} + 2e \\ \hline \underline{NiS} + 2NO_3^- + 4H^+ &= Ni^{++} + 2NO_2 + 2H_2O + \underline{S} \end{aligned}$$

The best test for nickel is the reaction with dimethylglyoxime, which forms a flocculent red precipitate of nickel dimethylglyoxime. The test is usually conducted with an alcoholic, 10 per cent solution of the reagent, in a solution faintly alkaline with ammonia. The reaction may be written in empirical form:

$$2[(CH_3)_2(CNOH)_2] + Ni^{++} + 2OH^- = Ni[(CH_3)_2(CNOH)(CNO)]_2 + 2H_2O$$

The formation of the nickel compound can be best shown by the written equation in graphic form.



See page 86 for a discussion of the structure of this chelate compound.

This delicate test for nickel is the basis for the best method for the quantitative determination of nickel. Cobalt ions do not react in this manner, therefore this reaction is used as a test for nickel in the presence of cobalt.

A bead of fused borax, when touched to a bit of powdered nickel salt and held in the oxidizing part of the flame of a Bunsen burner, will be colored a reddish brown. Borax, when fused, undergoes decomposition, probably according to the reaction:

$$Na_2B_4O_7 \cdot 10H_2O \rightarrow B_2O_3 + 2NaBO_2 + 10H_2O$$

forming a solid solution of boron trioxide in sodium metaborate. The nickel salt, such as $Ni(NO_3)_2$, likewise decomposes when heated to form NiO, which then reacts with the B_2O_3 to form nickel metaborate:

$$NiO + B_2O_3 = Ni(BO_2)_2$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Nickel Solution. To 5 ml. of nickelous nitrate test solution, add drop by drop a dilute solution of NH_4OH. Note that a greenish precipitate first forms. What is it? Give the equation for the reaction by which it is formed. Continue the slow addition of ammonia reagent until the precipitate dissolves, forming a solution which now contains the nickel in the form of tetrammono-nickel ions. Write the reaction.

Effect of NH_4Cl. To 5 ml. of test solution, add a quantity of NH_4Cl, and then slowly add NH_4OH. What happens? Explain the function of the NH_4Cl.

The effect of NH_4Cl on the solubility of the basic nickel compound should also be shown by precipitating a quantity of the basic salt and observing that it dissolves when sufficient NH_4Cl is present.

Precipitation of Nickelous Sulfide, NiS. Pass into the solution containing the deep blue complex ions a stream of H_2S. The first action of H_2S is to neutralize an equivalent amount of NH_4OH, producing thereby a rather high sulfide-ion concentration. The sulfide ion then reacts with the complex nickel ion, precipitating NiS. Show these steps by suitable equations.

Filter off the NiS. The filtrate is sometimes brown, owing to the presence of colloidal nickel sulfide; the presence of NH_4Cl during the precipitation aids considerably in lessening the tendency toward colloidal formation.

2. Action of Acids on NiS. Treat some of the NiS with a few milliliters of 1:9 HCl (made by adding 90 ml. of water to 10 ml. of concentrated HCl; reserve the remainder of this reagent for corresponding experiments with other members of this group). Does the precipitate appear to dissolve?

To the remainder of the NiS add aqua regia. Does the sulfide readily dissolve? Write the equation for the reaction. The sulfur which separates is usually of a gummy nature and may be discolored by some undissolved nickel sulfide.

3. Test with Dimethylglyoxime. To a solution of $Ni(NO_3)_2$, made faintly ammoniacal with NH_4OH, add a few drops of dimethylglyoxime reagent. Describe the result. Ascertain the structure of the precipitate which forms.

4. Borax Bead Test. Seal a piece of platinum wire in the end of a glass tube (if this has not already been done). Make a small loop in the end of the platinum wire. Heat the loop to redness, touch it to a quantity of borax, and fuse it in the flame of a Bunsen burner. The operation may have to be repeated until a bead somewhat larger than a pinhead is obtained.

Allow the clear bead to cool, moisten it and dip it into a very small quantity of powdered $Ni(NO_3)_2$. Then hold it in the oxidizing (outside) portion of the flame and observe the result.

COBALT, Co^{++}

Cobalt, like nickel, may be either divalent or trivalent in its compounds. The divalent, cobaltous salts are commoner and in solution are pink. Cobaltous hydroxide, $Co(OH)_2$, is pink, changing by oxidation to brown cobaltic hydroxide. Like the hydroxides of nickel and iron, the hydroxides of cobalt are not amphoteric. Many complex salts of cobalt are known, of which the most important types are those formed with ammonia, cyanide and nitrite. The cobaltous ion, in many of its reactions, resembles the nickelous ion.

Ammonia solution, when added in equivalent amount to a cobaltous salt solution, produces a greenish blue basic salt. Thus, with $Co(NO_2)_3$ test solution the reaction is:

$$Co^{++} + NO_3^- + OH^- = \underline{Co(OH)NO_3}$$

An excess of the reagent will dissolve the precipitate, forming a

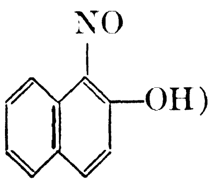
brownish solution of the hexammono-cobaltous ion:

$$\underline{Co(OH)NO_3} + 6NH_3 = Co(NH_3)_6^{++} + OH^- + NO_3^-$$

On heating and exposure, this complex ion passes over into the complex, $Co(NH_3)_6^{+++}$, with change in color to pinkish purple. If NH_4Cl is present when ammonia is added, the $Co(NH_3)_6^{++}$ forms directly.

Cobaltous sulfide, CoS, is best precipitated by H_2S from solutions of cobaltous salts which are made alkaline with ammonia. The sulfide is black. It does not form colloidal solutions like NiS. CoS, like the corresponding NiS, is practically insoluble in dilute HCl but is readily dissolved by concentrated HNO_3 or aqua regia. For the equation, see the corresponding reaction under "Nickel."

A delicate test for cobalt is by use of the organic reagent, α-nitroso-β-naphthol. This reagent first oxidizes the cobalt ion to the trivalent, cobaltic state. Then the hydrogen atoms from the hydroxyl groups from three molecules of the substance, as shown in the structural formula of the reagent, are replaced by a trivalent cobalt atom, forming cobaltic nitroso-β-naphthol:

3() + Co^{+++} = $\underline{Co[C_{10}H_6(NO)O]_3}$ + $3H^+$

The precipitate has a reddish purple color. The reagent is a 50 per cent acetic acid solution of the compound. Nickel ion does not yield a precipitate with this reagent, hence the test for cobalt can be conducted in the presence of nickel.

Another test for cobalt is the reaction with KNO_2. This reagent precipitates from acetic acid solutions a yellow compound, potassium cobaltinitrite, $K_3Co(NO_2)_6$. To carry out this test, the solution should be concentrated to a small volume, acidified with dilute acetic acid, saturated with KCl; then KNO_2 should be added in excess. The acetic acid liberates HNO_2, which decomposes with the formation of NO. The cobalt is oxidized to $Co(NO_2)_3$, which reacts with KNO_2 to form $K_3Co(NO_2)_6$. This test for cobalt can be made in the presence of nickel.

A borax bead will be colored a rich, deep blue when cobalt is present. The probable composition accounting for the color is

$Co(BO_2)_2$. See analogous property under "Nickel." This test will distinguish cobalt in the presence of moderate amounts of nickel.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Cobalt Solution. To 5 ml. of cobaltous nitrate test solution add, very slowly, dilute NH_4OH. The precipitate which forms first is not $Co(OH)_2$ but a basic salt similar to that of nickel. Give the reaction. Record the color.

Continue to add ammonia until the precipitate dissolves. The brownish solution contains complex ions whose composition is probably $Co(NH_3)_6^{++}$. Heat the solution containing the complex salt. The change in color is due to the formation of a hexammono-cobaltic complex of the probable composition, $Co(NH_3)_6^{+++}$.

Effect of NH_4Cl. To 5 ml. of test solution, add a quantity of NH_4Cl and then slowly add NH_4OH. Describe the result.

Precipitate some of the basic salt with NH_4OH and then add NH_4Cl. Note whether or not it dissolves.

Precipitation of Cobaltous Sulfide, CoS. Into the solution containing the brown complex pass H_2S. Write the equation.

This result is equivalent to adding $(NH_4)_2S$ directly to a solution of cobalt containing an excess of NH_4OH.

2. Action of Acids on Cobalt Sulfide. Transfer the CoS obtained above to a small evaporating dish and add 1 ml. of 1:9 HCl. Does it dissolve? Decant the solution and add 1 ml. of aqua regia. Write the equation for the reaction with this solvent.

3. Test with α-Nitroso-β-Naphthol. Acidify a few milliliters of cobalt test solution with dilute HCl, warm and then add a few drops of nitroso-β-naphthol reagent. Note the color of the precipitate and record its formula.

4. Borax Bead Test. Fuse some cobalt salt with borax held in the loop of a platinum wire. A blue bead of cobalt metaborate of the probable composition $Co(BO_2)_2$ should result. This test will distinguish cobalt in the presence of moderate amounts of nickel.

MANGANESE, Mn^{++}

The compounds of manganese of importance from an analytical standpoint are the divalent manganous salts such as $Mn(NO_3)_2$, $Mn(OH)_2$, MnS, etc.; the tetravalent compounds of which MnO_2 and $MnO(OH)_2$ are typical; manganates such as Na_2MnO_4 in

which this element has an apparent valence of +6 and the permanganates, especially $KMnO_4$, in which manganese has an apparent valence of +7 in the MnO_4^- anion.

Manganous hydroxide is formed when a solution of Mn^{++} is treated with NaOH or NH_4OH. The product of the reaction, $Mn(OH)_2$, white when first formed, rapidly changes through partial oxidation to a brown basic oxide whose composition may be represented by the formula $MnO(OH)_2$:

$$\underline{Mn(OH)_2} + O_2 = \underline{2Mn(OH)_2}$$

This product may also be considered to be hydrated manganese dioxide, $MnO_2 \cdot H_2O$; or, when written H_2MnO_3, it is manganous acid. As manganous acid it may react further with $Mn(OH)_2$ to produce Mn_2O_3:

$$\underline{Mn(OH)_2} + \underline{H_2MnO_3} = Mn_2O_3 + 2H_2O$$

This latter product is in fact manganous manganite, $MnMnO_3$, i.e., the manganese salt of manganous acid.

The hydroxide is insoluble in an excess of NH_4OH or added NH_4Cl. In this respect, manganese differs from nickel, cobalt and zinc, since it does not form a complex ion with ammonia.

In an excess of NaOH, $Mn(OH)_2$ is insoluble. This means that it is not amphoteric in the sense that $Al(OH)_3$, $Cr(OH)_3$ and $Zn(OH)_2$ are. This difference in behavior serves to separate manganese and iron from aluminum, chromium and zinc and is the method of separation used in the systematic procedure.

Manganese sulfide, MnS, is best precipitated from an alkaline solution by H_2S or $(NH_4)_2S$. It is pink in color when first formed but changes gradually to the brownish hydrated form. The sulfide is soluble in dilute HCl.

Sodium peroxide readily oxidizes the manganous ion to the tetravalent state, forming $MnO(OH)_2$, in quite the same way as atmospheric oxygen. The equation for the oxidation of $Mn(OH)_2$ by Na_2O_2 may be formulated in the following way:

$$Na_2O_2 + 2H_2O + 2e = 2Na^+ + 4OH^-$$

$$\underline{Mn(OH)_2} + 2OH^- = MnO(OH)_2 + H_2O + 2e$$

$$\underline{Mn(OH)_2} + Na_2O_2 + H_2O = \underline{MnO(OH)_2} + 2Na^+ + 2OH^-$$

Certain other oxidizing agents will accomplish the same result;

for example bromine, in alkaline solution, is sometimes used in analytical procedures for this purpose.

The oxidation of manganese to the hexavalent state is sometimes used as a test for this element. The oxidizing agent is $KClO_3$, the reaction being carried out in a fused sodium carbonate bead. Sodium manganate, Na_2MnO_4, green in color, is the oxidation product; the reaction may be expressed by the equation:

$$3MnO(OH)_2 + KClO_3 + 3Na_2CO_3 = 3Na_2MnO_4 + 3CO_2 + 3H_2O + KCl.$$

The corresponding ion, $MnO_4^{=}$, is the manganate ion, in which the manganese has an apparent valence of +6.

The oxidation of manganese to the permanganate form, MnO_4^-, is one of the most distinctive properties of this element as well as a most useful analytical reaction. The formation of the pink or purple ion is a very sensitive test for manganese and is, as well, the basis of several important quantitative methods of determination of this element. Among the oxidizing agents used for this purpose are sodium (meta) bismuthate, lead dioxide and ammonium persulfate.

The oxidation of Mn^{++} to MnO_4^- by $NaBiO_3$ is expressed by the two half-cell equations:

$$Mn^{++} + 4H_2O = 2MnO_4^- + 5Bi^{+++} + 7H_2O$$

and

$$BiO_3^- + 6H^+ + 2e = Bi^{+++} + 3H_2O$$

giving as the balanced equation:

$$2Mn^{++} + 14H^+ + 5BiO_3^- = MnO_4^- + 5Bi^{+++} + 7H_2O$$

Likewise, for the oxidation of $MnO(OH)_2$ by the same reagent we have:

$$2MnO(OH)_2 + 10H^+ + 3BiO_3^- = 2MnO_4^- + 3Bi^{+++} + 7H_2O$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Manganous Solution. To 5 ml. of $Mn(NO_3)_2$ test solution add dilute NH_4OH. Note how the precipitate gradually changes color. Give the equations for the formation and oxidation of the precipitate.

Determine whether excess NH_4OH or added NH_4Cl have any effect on the solubility of the precipitate. Compare the action

here with the effect of these reagents on nickel and cobalt test solutions.

Precipitation of Manganous Sulfide, MnS. Pass a stream of H_2S into a test tube containing $Mn(NO_3)_2$ test solution, made ammoniacal with NH_4OH. Write the equation. Note whether a change in color of the sulfide takes place and account for this change.

2. Action of Acids on MnS. Treat the precipitate obtained in the preceding experiment with 1:9 HCl. Does it dissolve? Do NiS and CoS readily dissolve in acid of this strength?

3. Action of NaOH and Na_2O_2 on Manganous Salts. To a few milliliters of $Mn(NO_3)_2$ test solution, add slowly a solution of NaOH. What is the substance formed? Try to dissolve it in an excess of the strong base. Is $Mn(OH)_2$ amphoteric?

Add a little sodium peroxide, dropping it from the tip of a spatula into the test tube. To what is the brown color due? Give the equation for this oxidation.

4. The Bead Test for Manganese. Fuse some Na_2CO_3 in the loop of a platinum wire and dip it into the brown solid obtained in experiment 3. Heat in a Bunsen flame until fusion takes place and then touch the fused bead to some powdered $KClO_3$ and heat again. To what is the green color due? Write the equation.

5. The Bismuthate Test. To 2 ml. of $Mn(NO_3)_2$ test solution add about 1 ml. of dilute HNO_3 and then drop into the tube a little powdered sodium bismuthate. Allow the suspended matter to settle and note the color of the solution. Write the equation for the reaction.

IRON, Fe^{++} and Fe^{+++}

Iron exists in its compounds either in the ferrous (divalent) or the ferric (trivalent) condition. The ferrous compounds are easily oxidized to the ferric condition. Solutions of ferrous salts are pale green or almost colorless and contain the ferrous ion, Fe^{++}; ferric solutions are yellowish red, owing to the color of the Fe^{+++} ion. Ferrous salts are good reducing agents and ferric salts are fairly good oxidizing agents.

When a solution of a ferrous salt is treated with either NaOH or NH_4OH, ferrous hydroxide, $Fe(OH)_2$, precipitates. This is insoluble in an excess of either reagent. Ferric hydroxide, $Fe(OH)_3$, likewise precipitates when an alkaline reagent is added to a ferric salt solution. It is insoluble in both reagents.

With hydrogen sulfide, Fe^{++} precipitates black FeS. Ammonium sulfide acts in a similar manner. In the case of the ferric ion, H_2S first reduces Fe^{+++} to Fe^{++}, which then precipitates as FeS. Ammonium sulfide in an alkaline solution forms Fe_2S_3 with the ferric ion.

When Fe_2S_3 is treated with an acid such as HCl it dissolves, forming Fe^{++} and free sulfur:

$$\underline{Fe_2S_3} + 4H^+ = 2Fe^{++} + \underline{S} + 2H_2S$$

Sodium peroxide readily oxidizes ferrous compounds to the ferric state. With $Fe(OH)_2$ the following reaction takes place:

$$\underline{2Fe(OH)_2} + Na_2O_2 + 2H_2O = 2Fe(OH)_3 + 2Na^+ + 2OH^-$$

It is insoluble in an excess of NaOH. Ferric hydroxide likewise is insoluble in excess NaOH.

The reactions of ferrous and ferric ions with the complex iron cyanides are important analytically though somewhat confusing to the beginning student.

With ferric-ion and potassium ferrocyanide the reaction product is Prussian blue; the equation is:

$$4Fe^{+++} + 3Fe(CN)_6^{----} = Fe_4[Fe(CN)_6]_3$$

With ferric ions and potassium ferricyanide, $K_3Fe(CN)_6$, a brown solution first forms, but this soon oxidizes in the air, becoming blue because of the formation of Prussian blue.

Finally, ferrous ions with potassium ferricyanide yield also a blue precipitate, $Fe_3[Fe(CN)_6]_2$, which is ferrous ferricyanide, better known as Turnbull's blue:

$$2Fe(CN)_6^{\equiv} + 3Fe^{++} = \underline{Fe_3[Fe(CN)_6]_2}$$

These results are here tabulated:

Ion	*Ferrocyanide* $[Fe(CN)_6^{----}]$	*Ferricyanide* $[Fe(CN)_6^{\equiv}]$
Fe^{++}	$K_2Fe[Fe(CN)_6]$ white → blue	$Fe_3[Fe(CN)_6]_2$ Turnbull's blue
Fe^{+++}	$Fe_4[Fe(CN)_6]_3$ Prussian blue	$Fe[Fe(CN)_6]$ brown

A very delicate test for ferric iron is the reaction with thiocyanate ions, CNS^-, using NH_4CNS as reagent. The solution

becomes deep red in color owing to the presence of a complex ion of the probable composition, $Fe(CNS)_6^{\equiv}$. Nitric acid gives the same color with this reagent, and certain substances like phosphates, borates and alkali acetates interfere with the reaction in neutral solutions.

Phosphates in ammoniacal, neutral, or slightly acid solutions precipitate Fe^{+++} ions as ferric phosphate, $FePO_4$. If $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$ is added the precipitation of the phosphate is complete:

$$Fe^{+++} + HPO_4^{=} + C_2H_3O_2^{-} = \underline{FePO_4} + HC_2H_3O_2$$

If phosphates are present in mixtures being analyzed and are not removed, a part of the Group III precipitate will consist of $FePO_4$. This is again referred to in Part IV.

Acetates, when added in excess to an acetic acid solution of ferric iron, turn the solution red owing to the formation of non-ionized ferric acetate:

$$Fe^{+++} + 3C_2H_3O_2^{-} = Fe(C_2H_3O_2)_3$$

This reaction is utilized in the phosphate removal discussed in Part IV. Ferric acetate hydrolyzes in dilute solution upon boiling:

$$Fe(C_2H_3O_2)_3 + 2HOH = \underline{Fe(OH)_2(C_2H_3O_2)} + 2HC_2H_3O_2$$

forming insoluble basic ferric acetate. This reaction is often used in analytical chemistry.

PRELIMINARY EXPERIMENTS

1. **Action of Group Reagent on Ferric Solution.** To 5 ml. of ferric nitrate, $Fe(NO_3)_3$, test solution add dilute NH_4OH. Observe the nature of the precipitate formed. Write the equation.

Add an excess of the reagent. Is the behavior different from that of nickel and cobalt? Add some NH_4Cl to the $Fe(OH)_3$, shake and warm. Does the precipitate dissolve?

Precipitation of Fe_2S_3. Pass H_2S into the test tube containing the ferric hydroxide, excess of NH_4OH and NH_4Cl. Write the equation for the reaction that takes place.

2. **Action of Acids on Fe_2S_3.** Treat the ferric sulfide obtained in the preceding experiment with 1:9 HCl. Show by an equation how the ferric ion is reduced during the dissolving process. To what is the turbidity due?

3. Action of NaOH and Na_2O_2. To a ferrous salt solution add dilute NaOH until the solution is strongly alkaline. What is the precipitate which forms? Is it soluble in excess of NaOH?

Add a little sodium peroxide to the test tube. What happens? Write the equation. Determine whether the product which forms is soluble in an excess of NaOH. Keep this in mind when similar experiments are performed with $Al(OH)_3$, $Cr(OH)_3$ and $Zn(OH)_2$.

4. Prussian Blue Test for Ferric Iron. Filter off the ferric hydroxide obtained above, dissolve it in dilute HCl and to a part of the solution add a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$, reagent. Write the equation.

Repeat the experiment, using potassium ferricyanide, $K_3Fe(CN)_6$, instead of the ferrocyanide. Note the result.

ALUMINUM, Al^{+++}

The most characteristic property of aluminum is the ease with which its salts hydrolyze to form insoluble aluminum hydroxide. $Al(OH)_3$ shows the property of amphoterism to a marked extent. The common salts such as the chloride, nitrate and sulfate are soluble in water. The Al^{+++} ion is colorless. Aluminum in all its compounds is always trivalent, hence aluminum salts are subject to neither oxidation nor reduction.

Ammonium hydroxide when added to a solution containing the Al^{+++} ion precipitates white gelatinous $Al(OH)_3$. The precipitate is practically insoluble in an excess of the reagent, resembling in this respect $Fe(OH)_3$, $Cr(OH)_3$ and $Mn(OH)_2$ and differing from the hydroxides of nickel, cobalt and zinc which form complex ammonia ions. Boiling and the presence of NH_4Cl aid in the more complete precipitation of $Al(OH)_3$.

Aluminum hydroxide rather than Al_2S_3 forms when an ammoniacal solution of Al^{+++} is treated with H_2S or $(NH_4)_2S$. The result is due to hydrolysis, the reaction being expressed by the equation:

$$Al_2S_3 + 6HOH = \underline{2Al(OH)_3} + 3H_2S$$

$Al(OH)_3$ is a typical amphoteric hydroxide which dissolves in strong acids as well as alkalies. Thus, when an excess of NaOH is added to Al^{+++} solution, the $Al(OH)_3$ first formed reacts to

form the meta-aluminate ion:

$$Al\begin{matrix} \diagup OH \\ -OH \\ \diagdown OH \end{matrix} + OH^- + Na^+ \rightarrow Na^+ + AlO_2^- + 2H_2O$$

If a solution of the aluminate ion is carefully neutralized with dilute HCl, the hydroxide reprecipitates:

$$AlO_2^- + H^+ + H_2O = \underline{Al(OH)_3}$$

The dissolving of $Al(OH)_3$ in acids such as HCl can be indicated by the equation:

$$\underline{Al(OH)_3} + 3H^+ = Al^{+++} + 3H_2O$$

A sensitive test for aluminum is the formation of an adsorption complex or " lake " with the dye " Aluminon," the trade name for the ammonium salt of aurin-tricarboxylic acid. This dyestuff is strongly adsorbed by $Al(OH)_3$ producing a bright red color. Alizarin and alizarin-S are two other dyes which produce lakes similar to Aluminon with aluminum hydroxide.

Another test for aluminum is known as " Thenard's Blue " test. This consists of igniting a roll of filter paper impregnated with $Co(NO_3)_2$ and $Al(OH)_3$, whereby a blue-colored residue is produced. This product is probably a cobalt aluminate. Details for carrying out the test are given later.

Phosphates will precipitate $AlPO_4$, which is soluble in bases as well as strong acids but insoluble in dilute acetic acid. Acetates will form $Al(C_2H_3O_2)_3$, easily hydrolyzed in dilute, boiling solution to the basic acetate, $Al(OH)_2(C_2H_3O_2)$. These properties must be kept in mind in the analysis of Group III when phosphates are present.

Tartrates, citrates, sugars and many other organic substances of similar composition prevent the precipitation of $Al(OH)_3$ by forming complex aluminum-organic ions. Such interfering substances must be removed in systematic analysis.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Aluminum Solution. Add dilute NH_4OH to 5 ml. of the $Al(NO_3)_3$ test solution. What forms? Add an excess of NH_4OH. Is the precipitate noticeably soluble in this reagent?

Action of NH_4Cl. To 5 ml. of test solution, add some NH_4Cl and then dilute NH_4OH slowly at first and then in excess. Does the precipitate dissolve? What is the function of the NH_4Cl?

Action of H_2S. Pass H_2S into 5 ml. of the test solution made ammoniacal with dilute NH_4OH. The precipitate is $Al(OH)_3$ and not Al_2S_3 as might be expected. Explain why $Al(OH)_3$ forms. Write the equation.

2. Amphoteric Nature of $Al(OH)_3$. Add dilute NaOH dropwise to 2 ml. of test solution. Note that $Al(OH)_3$ is at first precipitated. Then add more NaOH. What happens? Give the equation.

Carefully neutralize the aluminate solution with dilute HCl. What forms? Add more HCl and record what happens.

3. Thenard's Blue Test for $Al(OH)_3$. Take a strip of rolled filter paper, dip it in $Co(NO_3)_2$ solution, touch it to precipitated $Al(OH)_3$ and strongly heat it. Note the color of the ash.

4. "Aluminon" Test. Precipitate some $Al(OH)_3$ by adding NaOH to the test solution. Dissolve the precipitate in the least possible amount of dilute HCl, add 2 ml. of ammonium acetate solution and then 2 ml. of the "Aluminon" reagent. Mix thoroughly and then make ammoniacal with dilute NH_4OH. Observe the change in color.

CHROMIUM, Cr^{+++}

Chromium as cation forms the relatively unimportant chromous salts, such as $CrCl_2$ in which the element is divalent, and the chromic salts, for example, $CrCl_3$ and $Cr(NO_3)_3$, which contain trivalent chromium and in solution furnish the green chromic ion, Cr^{+++}. The test solution used in the laboratory is chromic nitrate.

In the form of chromates and dichromates the element exists in the hexavalent state as the anions $CrO_4^{=}$ and $Cr_2O_7^{=}$. In acidified solutions the chromate ion becomes the dichromate ion:

$$2CrO_4^{=} + 2H^+ = Cr_2O_7^{=} + H_2O$$

In alkaline medium the reverse takes place, the dichromate changing to chromate:

$$Cr_2O_7^{=} + 2OH^- = 2CrO_4^{=} + H_2O$$

Whether the chromate or the dichromate ion predominates depends therefore upon the alkalinity or acidity of the solution.

Chromate solutions are yellow and dichromate solutions are reddish-orange in color.

Ammonium hydroxide will precipitate from a chromic solution green, gelatinous chromic hydroxide, $Cr(OH)_3$. This hydroxide, like $Fe(OH)_3$ and $Al(OH)_3$, is practically insoluble in an excess of ammonia or in the presence of ammonium salts; it hence does not form complex ammonia ions, as do nickel, cobalt and zinc.

If H_2S or $(NH_4)_2S$ is added to an ammoniacal solution of the chromic ion, $Cr(OH)_3$ instead of Cr_2S_3 is formed, the result being due to hydrolysis. This behavior is like that of aluminum. Hence when a chromic solution is treated with NH_4OH, NH_4Cl and H_2S, the net result is the precipitation of $Cr(OH)_3$.

Chromic hydroxide is readily soluble in dilute HCl:

$$Cr(OH)_3 + 3H^+ = Cr^{+++} + 3H_2O$$

Sodium hydroxide, like NH_4OH, precipitates $Cr(OH)_3$:

$$\underline{Cr^{+++}} + 3OH^- = \underline{Cr(OH)_3}$$

An excess of the strong base, however, causes the precipitate to dissolve, forming the metachromite ion:

$$\underline{Cr(OH)_3} + 3OH^- = CrO_2^- + 2H_2O$$

The fact that chromic hydroxide dissolves in strong bases as well as in acids shows the amphoteric behavior of this substance.

Trivalent chromium, as, for example, the chromite ion and the chromic ion, are oxidized to $CrO_4^{=}$ by a number of oxidizing agents, such as sodium peroxide. With Na_2O_2 in an alkaline solution, the oxidation can be shown by the equation:

$$\begin{array}{r} 2[CrO_2^- + 4OH^- = CrO_4^{=} + 2H_2O + 3e] \\ 3[Na_2O_2 + 2H_2O + 2e = 2Na^+ + 4OH^-] \\ \hline 2CrO_2^- + 3Na_2O_2 + 2H_2O = 2CrO_4^{=} + 6Na^+ + 4OH^- \end{array}$$

Conversely, chromates and dichromates are reduced to the chromic ion by reducing agents. H_2S is such a reagent and, consequently, if chromates or dichromates are present in mixtures undergoing analysis, they will be reduced in an *acid* medium according to the reaction:

$$Cr_2O_7^{=} + 3H_2S + 8H^+ = 2Cr^{+++} + \underline{3S} + 7H_2O$$

The $CrO_4^{=}$ ion is precipitated by various cations forming compounds such as Ag_2CrO_4, $PbCrO_4$ and $BaCrO_4$. The precipitation of the latter is the means employed in the scheme of this group to separate chromium from zinc.

In addition to observations of the characteristic color changes undergone by chromium during its separation from other members of this group — observations which usually are sufficient to identify this element — the hydrogen peroxide test, described as experiment 5 under "Preliminary Experiments," may be employed.

Phosphates precipitate chromium phosphate, $CrPO_4$, from solutions containing chromic salts; in this respect they are similar in their behavior toward aluminum and ferric iron solutions. Acetates will precipitate basic chromic acetate only in the presence of large amounts of iron or aluminum. Tartrates and similar organic materials will prevent the precipitation of $Cr(OH)_3$ on account of the formation of complex ions. These properties are important in the systematic analysis of materials and are again referred to in Part IV, pages 309 to 311.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Chromic Solution. To 5 ml. of chromic nitrate test solution add dilute NH_4OH. What is the pale green gelatinous precipitate? Write the reaction in ionic form. Try to dissolve the chromic hydroxide in an additional amount of NH_4OH.

Action of NH_4Cl. To 5 ml. of test solution, add some NH_4Cl and then dilute NH_4OH slowly at first and then in excess. Does the precipitate appear to dissolve? In this respect it resembles the hydroxides of aluminum, iron and manganese, and differs from those of nickel, cobalt and zinc.

Action of H_2S. Pass H_2S into a few milliliters of test solution, made ammoniacal with ammonia. Explain what happens. Is the precipitate Cr_2S_3? Add dilute HCl (1:9) to the test tube containing precipitated $Cr(OH)_3$. Note result.

2. Amphoteric Nature of $Cr(OH)_3$. To 2 ml. of $Cr(NO_3)_3$ solution add, slowly, a dilute solution of NaOH until a precipitate forms. What is it?

Continue the addition of the NaOH until the precipitate redissolves. Write the equation. The dissolving of $Cr(OH)_3$ in NaOH to form the CrO_2^- ion follows the behavior of $Al(OH)_3$ and

$Zn(OH)_2$; this property is used to separate these three elements from iron and manganese.

Oxidation of Chromite to Chromate. Add to the sodium chromite solution a small quantity of Na_2O_2. Note the change of color from green to yellow. What has happened? Write the equation.

3. Precipitation of $BaCrO_4$. Neutralize a portion of the chro mate solution obtained in experiment 2 and then make it slightly acid with $HC_2H_3O_2$. Add a little $NaC_2H_3O_2$ and finally add $BaCl_2$. What forms? Supply the equation. This reaction enables one to separate chromium from zinc.

4. The Hydrogen Peroxide Test for $CrO_4^{=}$. To 1 ml. of $CrO_4^{=}$ solution acidified with dilute HNO_3 add 1 ml. of ether and then, dropwise, some hydrogen peroxide. Note the intense blue color in the ether layer; note also that it fades out quickly. The substance formed is of indefinite composition, probably a complex of CrO_4 and H_2O_2, though sometimes referred to as a perchromic acid.

ZINC, Zn^{++}

The element zinc is always divalent in its compounds. The zinc ion is colorless. The oxide, ZnO, and hydroxide, $Zn(OH)_2$, and salts such as $ZnCl_2$, $Zn(NO_3)_2$, ZnS and $ZnNH_4PO_4$ are among its important analytical compounds.

The hydroxide, $Zn(OH)_2$, is formed when either NH_4OH or $NaOH$ is added in equivalent amounts to a solution containing zinc ion.

In an excess of ammonia, $Zn(OH)_2$ dissolves to form a complex ion:

$$\underline{Zn(OH)_2} + 4NH_3 = Zn(NH_3)_4^{++} + 2OH^-$$

With an excess of NaOH or KOH, the hydroxide dissolves to form the zincate ion:

$$\underline{Zn(OH)_2} + 2OH^- = ZnO_2^{=} + 2H_2O$$

Zinc hydroxide is likewise soluble in acids. Like $Al(OH)_3$ and $Cr(OH)_3$, this hydroxide is typically amphoteric.

When H_2S is passed into a solution of zinc ions, white ZnS is precipitated:

$$Zn^{++} + H_2S = \underline{ZnS} + 2H^+$$

The sulfide, however, will not form if the acidity of the solution is equal to or greater than that prevailing for the precipitation of

the sulfides of Group II. It is best to buffer the solution with $NaC_2H_3O_2$ in order to secure complete precipitation of the sulfide.

Ammonium sulfide will precipitate ZnS from neutral or alkaline solutions.

Zinc sulfide is soluble in dilute HCl but does not dissolve in acetic acid.

As tests for zinc the following properties may be employed. When cobalt nitrate is impregnated on a filter paper along with a zinc compound and the paper is ignited, it leaves a green mass, known as Rinnman's Green, probably a cobalt zincate or a double oxide of CoO and ZnO. The details of carrying out this test are given in experiment 3.

Potassium ferrocyanide precipitates $Zn_3K_2[Fe(CN)_6]_2$ and this is sometimes used as a confirmatory test for zinc.

The test with the dyestuff, Orange IV, is particularly sensitive if proper precautions are taken. The procedure is described below.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent on Zinc Test Solution. Add dilute NH_4OH dropwise to a few milliliters of $Zn(NO_3)_2$ test solution until a precipitate forms. Write the equation for the reaction. Add an excess of NH_4OH. What happens? Give the equation.

Action of NH_4Cl. To 5 ml. of the test solution add NH_4Cl and then NH_4OH. Does $Zn(OH)_2$ precipitate? Explain the result.

Precipitation of ZnS. Into this solution containing the complex zinc-ammonia ions pass H_2S. What is the white precipitate?

2. Amphoteric Nature of $Zn(OH)_2$. Dissolve the ZnS obtained in the above experiment in dilute HCl, boil and then add a few drops of NaOH. Note the precipitation of $Zn(OH)_2$. Continue adding NaOH until the precipitate dissolves. Like $Al(OH)_3$ and $Cr(OH)_3$, zinc hydroxide is amphoteric and, with an excess of strong base, forms zincate ions. Write the equation.

3. Rinnman's Green Test. Cobalt nitrate when heated with ZnO forms a green-colored mass on the ignited filter paper. The color is due to a double oxide, ZnO·CoO, and is known as Rinnman's Green. This test can be most conveniently carried out by using specially prepared cobalt cyanide test paper.

4. The Orange IV Test for Zinc. To a drop of the dyestuff, known as Orange IV, add one drop of dilute (1:24) H_2SO_4 (both

reagents dispensed by the instructor) on a spot plate or watch glass or in a test tube, and then 3 to 5 drops of a 2 per cent solution of potassium ferricyanide. The mixture now should have a red color. Then add to this mixture a drop or two of the zinc test solution. The color should change to greenish yellow in the presence of zinc.

REVIEW EXERCISES — SET 13

1. Make a table showing the valences of the elements of this group, together with names, formulas and colors of typical compounds.

2. Group together the reactions of the cations of this group with NH_4OH; with NH_4OH in the presence of NH_4Cl; with $(NH_4)_2S$. Show that the net effect is a set of ionic reactions between these cations and $S^{=}$ ion (or HOH in two cases).

3. What sulfides of this group remain practically insoluble in 1:9 HCl? How does this suggest a method of subdivision?

4. Group together the reactions of the cations of this group with NaOH. Do all the hydroxides dissolve in excess NaOH? Complete and balance the following equations:

$$Mn(OH)_2 + NaOH =$$
$$Fe(OH)_2 + NaOH =$$
$$Al(OH)_3 + NaOH =$$
$$Cr(OH)_3 + NaOH =$$
$$Zn(OH)_2 + NaOH =$$

5. What products form when Na_2O_2 is dissolved in water? Complete and balance the following equations:

$$Mn(OH)_2 + Na_2O_2 + H_2O =$$
$$Fe(OH)_2 + Na_2O_2 + H_2O =$$
$$NaCrO_2 + Na_2O_2 + H_2O =$$

Why would you not expect $NaAlO_2$ and Na_2ZnO_2 solutions to react with Na_2O_2? How do the answers to questions 4 and 5 suggest a basis for further subdivision of members of this group? Explain your answer.

6. If a certain solution contains Al^{+++}, Zn^{++} and $CrO_4^{=}$ ions what reagent might be used to make a separation of aluminum from zinc and chromium? Show this by appropriate equations.

7. What hydroxides of this group show amphoteric behavior? Form complex ammonia ions? Are readily oxidized or reduced? Show marked hydrolysis of their salts?

8. Show by a set of ionization reactions why solutions of $FeCl_3$ show an acid reaction; why solutions of Na_2CO_3 show an alkaline reaction.

9. Explain why NiS and CoS are practically insoluble in 1:9 HCl, yet fail to be precipitated in Group II where the acidity is much less.

10. What organic reagent will precipitate nickel in the presence of cobalt? What reagents might be used to precipitate cobalt in the presence of nickel?

Outline of Method of Analysis of this Group

As a result of the study of the properties of the ions of this group, the following facts have been revealed:

1. The net effect of adding NH_4OH, NH_4Cl and H_2S to solutions containing these ions is to precipitate NiS, CoS, FeS or Fe_2S_3, $MnO(OH)_2$, ZnS and $Al(OH)_3$ and $Cr(OH)_3$. The intermediate formation of the complex ammonia ions of nickel, cobalt and zinc is incidental. The formation of $Al(OH)_3$ and $Cr(OH)_3$ rather than the sulfides of these two elements is due to hydrolysis.
2. Hydrochloric acid (1:9) was found to be an effective solvent for all the above precipitates except NiS and CoS. This reagent is therefore employed to separate these two sulfides from the other sulfides and hydroxides of this group.
3. The combined action of NaOH and Na_2O_2 was found to precipitate the iron as $Fe(OH)_3$ and the manganese as $MnO(OH)_2$, whereas, on account of strong amphoteric behavior, the aluminum, chromium and zinc are transformed into the meta-aluminate ion, AlO_2^-, the zincate ion, $ZnO_2^=$, and the chromate ion, $CrO_4^=$. This serves to separate the former two elements from the latter three.
4. If HNO_3 and then NH_4OH are added to solutions containing, respectively, AlO_2^-, $CrO_4^=$ ions, $Al(OH)_3$ only will be precipitated. In this we have a method of separating aluminum from chromium and zinc.
5. The precipitation of $BaCrO_4$ from a buffered acetic acid solution is utilized in the procedure of analysis as a means of separating chromium from zinc.

These indicated separations of the group precipitate, together with the necessary subsequent treatment of the separated portions for the purpose of individual cation identifications, are combined and shown diagrammatically as a scheme of analysis on page 193. The detailed procedure to be followed in the analysis of a mixture of ions of this group follows.

Practice Analysis of a Mixture of Cations of this Group

Prepare a mixture by taking 5 ml. of each of the test solutions of Ni^{++}, Co^{++}, Fe^{+++}, Mn^{++}, Al^{+++}, Cr^{+++} and Zn^{++}. Place the sample in an Erlenmeyer flask equipped with a stopper with inlet tube.

DIAGRAMMATIC SCHEME — GROUP III (Absence of Phosphates, Oxalates, etc.)

Solution: Ni^{++}, Co^{++}, Mn^{++}, Fe^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}, Zn^{++}

NH_4Cl added, made ammoniacal with NH_4OH; H_2S passed in; filtered.

Precipitate: NiS, CoS, MnS ($MnO(OH)_2$), FeS, Fe_2S_3, $Al(OH)_3$, $Cr(OH)_3$, ZnS

Treated with 1:9 HCl; filtered.

- **Residue:** NiS, CoS
  - Dissolved in aqua regia; boiled
  - Ni^{++} to one portion is added NH_4OH, 1 ml. dimethylglyoxime — red precipitate proves Ni. Co^{++} to one portion is added dilute HCl and 1 ml of α-nitroso-β-naphthol — red precipitate proves Co.
- **Filtrate:** Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}, Zn^{++}
  - Evaporated to 3 ml., diluted to 100 ml. Made alkaline with NaOH, Na_2O_2 added, boiled and filtered.
  - **Precipitate:** $MnO(OH)_2$, $Fe(OH)_3$
    - Dissolved one portion in 5 ml. concentrated HNO_3, PbO_2 added, boiled — pink supernatant color proves Mn.
    - Dissolved one portion in dilute HCl, $K_4Fe(CN)_6$ added — heavy blue precipitate proves Fe.
  - **Filtrate:** AlO_2^-, CrO_4^-, ZnO_2^-
    - Neutralized with HNO_3, NH_4Cl added, made ammoniacal with NH_4OH; filtered.
    - **Precipitate:** $Al(OH)_3$
      - White gelatinous precipitate, filter paper wrapped around platinum wire, moistened with $Co(NO_3)_2$, heated — blue color proves Al — Aluminon test.
    - **Filtrate:** CrO_4^-, $Zn(NH_3)_4^{++}$
      - Acidified with dilute $HC_2H_3O_2$; 1 gram $NaC_2H_3O_2$ added, heated and $BaCl_2$ added.
      - **Precipitate:** $BaCrO_4$
        - Dissolved in dilute HNO_3, 1 ml. H_2O_2 added — blue ether layer proves Cr.
      - **Filtrate:** Zn^{++}
        - H_2S passed in — white precipitate proves Zn. Orange IV test.

Group Precipitation. Make the solution ammoniacal with dilute NH_4OH and then add an excess of 2 ml. of concentrated NH_4OH. This will result in the precipitation of the hydroxides of iron, manganese, aluminum and chromium and in the formation of $Ni(NH_3)_4^{++}$, $Co(NH_3)_6^{+++}$ and $Zn(NH_3)_4^{++}$.

Heat the solution almost to boiling, stopper the flask and pass in a rapid stream of H_2S. The partial neutralization of the ammonium hydroxide by the hydrogen sulfide produces $(NH_4)_2S$ and furnishes a large concentration of sulfide ions. The final effect is the precipitation of the sulfides of nickel, cobalt, iron, zinc and manganese (the latter oxidizes to the basic oxide, $MnO(OH)_2$) and of $Al(OH)_3$ and $Cr(OH)_3$.

The net effect of the combined use of NH_4OH and H_2S is shown by the equations:

$$Ni^{++} + S^{=} = \underline{NiS}$$

$$Co^{++} + S^{=} = \underline{CoS}$$

$$2Fe^{+++} + 3S^{=} = \underline{Fe_2S_3}$$

$$Mn^{++} + S^{=} = \underline{MnS} \rightarrow \underline{MnO(OH)_2}$$

$$Zn^{++} + S^{=} = \underline{ZnS}$$

$$Al^{+++} + 3OH^{-} = \underline{Al(OH)_3}$$

$$Cr^{+++} + 3OH^{-} = \underline{Cr(OH)_3}$$

Filter a small portion of the solution and test the filtrate with H_2S for complete precipitation. If not complete, continue the use of H_2S a little while longer. When precipitation is complete, filter through a fluted filter or with the aid of a filtration accelerator. Wash the precipitate with hot water containing a small quantity of NH_4Cl. The ammonium chloride is used here and in the group precipitation to decrease the solubility of $Al(OH)_3$ and $Cr(OH)_3$ and to lessen the tendency toward the formation of colloidal sulfide solutions.

Separation of NiS and CoS. Transfer the washed group precipitate to a beaker and treat it with 50 ml. of dilute (1:9) HCl, made by adding 5 ml. of concentrated HCl to 45 ml. of water. Stir the mixture and allow to settle. *Do not heat.* In HCl of this strength NiS and CoS do not dissolve at an appreciable rate, whereas the

other constituents dissolve at once. The effect of the solvent can be shown by the equations:

$$\underline{NiS} + H^+ \rightarrow \underline{NiS} \text{ (no reaction)}$$

$$\underline{CoS} + H^+ \rightarrow \underline{CoS} \text{ (no reaction)}$$

$$\underline{MnO(OH)_2} + 4H^+ + 4Cl^- = Mn^{++} + 3H_2O + Cl_2 + 2Cl^-$$

$$\underline{Fe_2S_3} + 4H^+ = 2Fe^{++} + 2H_2S + \underline{S}$$

$$\underline{Al(OH)_3} + 3H^+ = Al^{+++} + 3H_2O$$

$$\underline{Cr(OH)_3} + 3H^+ = Cr^{+++} + 3H_2O$$

$$\underline{ZnS} + 2H^+ = Zn^{++} + H_2S$$

Filter off the residue, which consists of NiS and CoS. Place the filtrate in a large evaporating dish and begin the evaporation of the solution. While this is in progress remove the residue of nickel and cobalt sulfides to another evaporating dish, add a few milliliters of aqua regia (enough to dissolve the residue) and evaporate to a small volume, being watchful not to carry the evaporation to dryness.

Dilute with a few milliliters of dilute HCl and filter to remove the small residue of black, gummy sulfur. Now add, drop by drop, dilute NaOH until a permanent precipitate forms and then dissolve this in dilute acetic acid, adding a slight excess.

Identification of Nickel. Take 2 ml. of this solution, make it slightly ammoniacal with dilute NH_4OH, testing with litmus paper, and then add 1 ml. of dimethylglyoxime reagent. The heavy, red precipitate which forms is nickel dimethylglyoxime, $Ni[(CH_3)_2\text{-}CNOHCNO]_2$, and shows the presence of nickel.

Identification of Cobalt. To another 2 ml. portion of the solution add a little dilute HCl, warm and then add 1 ml. of α-nitroso-β-naphthol reagent. The reddish precipitate is cobaltic nitroso-β-naphthol, $Co(C_{10}H_6NOO)_3$, which identifies cobalt.

Confirm this by the cobaltinitrite test: To a portion of the solution, acid with acetic acid, add solid KCl until no more will dissolve and then add an equal volume of 50 per cent KNO_2 solution. Set the test aside and after an hour or so, examine it. The yellow precipitate is potassium cobaltinitrite, $K_3Co(NO_2)_6$.

Separation of Manganese and Iron. The filtrate from the separation of NiS and CoS, undergoing evaporation and containing Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++} and Zn^{++}, should be concentrated to a few milliliters to remove excess HCl. When this is done, dilute to about 100 ml. with water and make strongly alkaline with an excess of NaOH solution. Without filtering add cautiously, by means of a spatula, 2 grams of Na_2O_2 and boil the solution for a few minutes with frequent stirring.

By this treatment, the manganese is oxidized and precipitated as $MnO(OH)_2$, the iron likewise as $Fe(OH)_3$, and the remaining three elements are transformed into the soluble anions, namely, meta-aluminate, AlO_2^-, chromate, $CrO_4^=$, and zincate, $ZnO_2^=$. The effect of the use of Na_2O_2 is shown by the equations:

$$Mn^{++} + Na_2O_2 + H_2O_2 = \underline{MnO(OH)_2} + 2Na^+$$

$$2Fe^{++} + Na_2O_2 + 2OH^- + 2H_2O = \underline{2Fe(OH)_3} + 2Na^+$$

$$Al^{+++} + 4OH^- = AlO_2^- + 2H_2O$$

$$2Cr^{+++} + 4OH^- + 3Na_2O_2 = 2CrO_4^= + 2H_2O + 6Na^+$$

$$Zn^{++} + 4OH^- = ZnO_2^= + 2H_2O$$

Partly neutralize the solution with dilute HNO_3, filter and wash the precipitate. The filtrate is reserved for the identification of Al, Cr and Zn.

Identification of Manganese. Remove a small part of the brown precipitate to a test tube, dissolve it with 5 ml. of concentrated HNO_3 or, to hasten the dissolving, use in addition a few drops of hydrogen peroxide. To the solution add a small quantity of sodium bismuthate, $NaBiO_3$, shake and allow the suspended matter to settle. The pink or purple coloration in the supernatant liquid is due to the presence of the permanganate ion, MnO_4^-, and identifies manganese. In place of $NaBiO_3$, should this reagent not be available, lead peroxide, PbO_2, may be used, using 1 gram of this reagent.

A further test for manganese might well be made at this point. This is the bead test described on page 181. In the loop of a platinum wire fuse some Na_2CO_3, touch it to the brown precipitate of $MnO(OH)_2$, heat and then dip it into powdered $KClO_3$ and heat in the Bunsen flame. The green or greenish blue bead which derives

its color from sodium manganate, Na_2MnO_4, is a further proof of the presence of manganese.

Identification of Iron. Take another small portion of the precipitate, dissolve it in dilute HCl, cool and add a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$. The heavy, deep blue precipitate, Prussian blue, $Fe_4[Fe(CN)_6]_3$, identifies iron. An excess of the reagent is to be avoided because the product is soluble in an excess of the reagent.

The extremely delicate reaction with KCNS might also be applied here. This is carried out, quite simply, by dissolving a very tiny bit of the precipitate in dilute HCl and adding a drop of KCNS reagent, resulting in an intensely red-colored solution. This test should not be employed on samples of unknown composition such as the "student unknowns," since traces of iron, frequently present as impurities in reagents, will respond to this test.

Separation and Identification of Aluminum. The filtrate from the removal of iron and manganese contains AlO_2^-, $CrO_4^=$ and $ZnO_2^=$ ions together with excess NaOH.

Neutralize the alkali with dilute HNO_3. The addition of HNO_3 has the effect shown in the following equations:

$$AlO_2^- + 4H^+ = Al^{+++} + 2H_2O$$

$$2CrO_4^= + 2H^+ = Cr_2O_7^= + H_2O$$

$$ZnO_2^= + 4H^+ = Zn^{++} + 2H_2O$$

Add a little NH_4Cl and then make the solution slightly ammoniacal with dilute NH_4OH in order to precipitate $Al(OH)_3$. Avoid adding an excess of ammonia because $Al(OH)_3$ is somewhat soluble in an excess of this reagent. The solution should have only a slight odor of ammonia; if too much has been added, boil the solution.

The reactions taking place are:

$$Al^{+++} + 3OH^- = \underline{Al(OH)_3}$$

$$Cr_2O_7^= + 2OH^- = 2CrO_4^= + H_2O$$

$$Zn^{++} + 4NH_3 = Zn(NH_3)_4^{++}$$

Remove most of the gelatinous precipitate to a test tube, dissolve it with dilute HCl, add 3 ml. of ammonium acetate solution

and 5 ml. of "Aluminon" reagent. Mix thoroughly and then make the solution alkaline with dilute NH_4OH. The bright red color of the precipitated $Al(OH)_3$ identifies aluminum.

The formation of Thenard's blue as a test for aluminum should also be carried out. Proceed as follows: Tear off a portion of the filter paper which is coated with the precipitate, hold it in the loop of a platinum wire, moisten with a few drops of dilute $Co(NO_3)_2$ and ignite. A blue color in the charred paper, due to a double oxide, $CoO \cdot Al_2O_3$, known as Thenard's blue, shows the presence of aluminum. If the $Co(NO_3)_2$ solution is too strong black cobalt oxide may result.

Identification of Chromium. The filtrate after the separation of $Al(OH)_3$ contains $CrO_4^{=}$ and $Zn(NH_3)_4^{++}$ ions. The yellow color of this solution is a sure indication of the presence of the chromate ion. To remove the chromate ion and further identify it, acidify the solution with dilute $HC_2H_3O_2$, add 1 gram of $NaC_2H_3O_2$, heat to boiling and, while hot, add slowly $BaCl_2$ reagent. Allow the yellow $BaCrO_4$ to settle and then filter through two thicknesses of filter paper. Reserve the filtrate for the identification of zinc.

Dissolve the $BaCrO_4$ on the filter paper in dilute HNO_3, using warm acid if necessary. Add the filtrate to a test tube containing 1 ml. of ether and 1 ml. of 3 per cent H_2O_2. If chromium is present the ether layer will be blue.

Identification of Zinc. Zinc in the form of ionized $Zn(C_2H_3O_2)_2$ remains in the filtrate after removal of the $BaCrO_4$. This solution contains $HC_2H_3O_2$ and is buffered with $NaC_2H_3O_2$. Pass H_2S into this solution. ZnS should precipitate as a white, finely divided precipitate.

If the precipitate has a dark color, showing that traces of FeS, NiS or CoS have formed, add a little dilute HCl, filter and add a little Na_2O_2 to the filtrate. Again filter and discard the precipitate of $Fe(OH)_3$. Neutralize the filtrate with HNO_3, add a little $HC_2H_3O_2$ and $NaC_2H_3O_2$ and reprecipitate the ZnS.

ZnS can be further identified by a test similar to that for aluminum. Coat a portion of the filter paper with the white precipitate, moisten with $Co(NO_3)_2$, hold in a platinum wire and strongly ignite. A green color on the charred paper, a mixture of CoO and ZnO, proves the presence of zinc. Specially prepared test paper may also be used here.

Zinc can best be identified by means of the dye, Orange IV, as mentioned on page 190. Proceed as follows: Dissolve a portion of the ZnS precipitate in dilute H_2SO_4. To a drop of $K_3Fe(CN)_6$ on a watch glass or spot plate, add a drop of dilute 1:24 H_2SO_4 and then 3 to 5 drops of freshly prepared $K_3Fe(CN)_6$ solution. This will produce a red color. Then add a drop or two of the neutralized zinc solution; the green color shows the presence of zinc.

Application of Theory to the Analysis of this Group

This group furnishes a number of excellent examples illustrating several important principles. Among the principles involved are (1) the theory of sulfide precipitation, (2) hydrolysis, (3) common-ion effect, (4) complex-ion formation, (5) amphoterism and (6) oxidation-reduction phenomena. These will be discussed in turn.

Sulfide Precipitation. Previous discussion of the theory (see page 168) involved in the precipitation of sulfides disclosed the fact that the sulfides of this group are characterized by relatively large solubility product constants and that in order effectively to precipitate them the sulfide-ion concentration should be as high as possible. Such a concentration can be secured by the use of highly ionized sulfides such as $(NH_4)_2S$ or Na_2S. In the actual procedure used here, the ammonium sulfide is formed in the solution by the neutralization of NH_4OH by H_2S; in some procedures $(NH_4)_2S$ is added directly as reagent. The $K_{s.p.}$ values for the sulfides of this group are quickly reached and exceeded under these conditions, and precipitation is rapid and complete.

Hydrolysis. The sulfides of aluminum and chromium cannot exist in aqueous solutions because hydrolysis takes place. Hydrolysis results whenever the concentration of H^+ ions or OH^- ions or both can be lowered. The hydrolytic reaction will run practically to completion if both ions are removed. In the reaction:

$$Al_2S_3 + 6HOH = \underline{2Al(OH)_3} + \overline{3H_2S}$$

the hydroxyl ions are removed in the form of an insoluble precipitate and the hydrogen ions by the evolution of a gas. Al_2S_3, if formed, would at once completely hydrolyze. The addition of H_2S to basic solutions containing precipitated $Al(OH)_3$ is therefore without effect. The case of chromium is similar.

Common-Ion Effect. The solubility product constant of $Mg(OH)_2$ is 3.5×10^{-11}, a value which can easily be reached by such concentrations of Mg^{++} ions and OH^- ions in ammoniacal solutions as are used in analytical work. The precipitation of $Mg(OH)_2$ with the inclusion of magnesium as a member of this group is undesirable; therefore, it must be kept in solution during the group precipitation. By adding NH_4Cl to the NH_4OH of the group reagent, the NH_4^+ ions, through the common-ion effect, lower the OH^- ion concentration to such a value that the product, $C_{Mg^{++}} \times (C_{OH^-})^2 = 3.5 \times 10^{-11}$, is not reached. The required basic condition for the group precipitation is thus maintained, yet magnesium hydroxide is prevented from precipitating.

Common-ion effect is also employed in the separation of $BaCrO_4$ and in the reprecipitation of ZnS. In these cases the acidity of dilute acetic acid solutions is decreased through the addition of $NaC_2H_3O_2$ (the common acetate ions lower the H^+ ion in the acetic acid equilibrium).

Amphoterism. The amphoteric nature of $Zn(OH)_2$, $Cr(OH)_3$ and $Al(OH)_3$ is utilized to separate these three elements from iron and manganese. This behavior can be illustrated by zinc hydroxide. This compound exhibits a stronger basic character than acid character and its ionization can be considered as taking place chiefly in a basic direction thus:

$$Zn\begin{array}{l}\diagup OH \\ \diagdown OH\end{array} \rightarrow Zn^{++} + 2OH^-$$

The addition of an acid will neutralize the hydroxyl ions and cause the $Zn(OH)_2$ to dissolve, forming Zn^{++} ions in solution. If, however, a strong base, NaOH for example, is added, the hydrogen ions and not the hydroxyls are displaced:

$$Zn\begin{array}{l}\diagup OH \\ \diagdown OH\end{array} + 2OH^- = ZnO_2^{=} + 2H_2O$$

The zinc existing in solution is in the form of zincate, $ZnO_2^{=}$, ions. In analogous ways, aluminate and chromite ions are formed.

THE AMMONIUM CARBONATE GROUP—GROUP IV

BARIUM, Ba^{++}
STRONTIUM, Sr^{++}
CALCIUM, Ca^{++}

The alkaline earth elements, barium, strontium and calcium, are very much alike in their general properties and behavior. Their chlorides, sulfides and hydroxides are sufficiently soluble to prevent their precipitation in preceding groups. The salts of these elements which constitute the basis of the analysis of this group are the carbonates, chromates, sulfates and oxalates. The group as a whole is precipitated as $BaCO_3$, $SrCO_3$ and $CaCO_3$ with $(NH_4)_2CO_3$, in an ammoniacal solution containing NH_4Cl. The elements of this group are free from hydrolysis, amphoterism, complex-ion formation and oxidation and reduction effects; hence the separations from one another depend solely upon precipitation phenomena. Flame tests are relied upon for final identification.

Magnesium, a closely related element, whose carbonate and hydroxide are rather insoluble, is prevented from precipitating here, by buffering the group reagent with NH_4Cl. Certain schemes of analysis include magnesium in this group, but the procedure preferred here purposely keeps this ion from precipitating until Group V is reached.

BARIUM, Ba^{++}

This element is always divalent. The salts are colorless unless the anion is colored. The hydroxide is too soluble to be precipitated by NH_4OH or $NaOH$. Ammonium carbonate precipitates white $BaCO_3$:

$$Ba^{++} + CO_3^{=} = \underline{BaCO_3}$$

$BaCO_3$ is soluble in strong acids as well as weak acids, such as $HC_2H_3O_2$ and H_2CO_3. In the case of acetic acid, the bicarbonate ion, HCO_3^-, first forms:

$$\underline{BaCO_3} + H^+ = Ba^{++} + HCO_3^-$$

which then reacts to form unstable H_2CO_3:

$$HCO_3^- + H^+ = H_2CO_3 \rightarrow H_2O + CO_2$$

Barium chromate is precipitated when $CrO_4^{=}$ ions are added to a barium salt solution:

$$Ba^{++} + CrO_4^{=} = \underline{BaCrO_4}$$

$BaCrO_4$ is soluble in strong acids but insoluble in acetic acid. It is best precipitated from a solution buffered with $NaC_2H_3O_2$, whereby the H^+ ion concentration is diminished.

Barium sulfate is readily precipitated by dilute H_2SO_4 or a soluble sulfate such as $(NH_4)_2SO_4$.

$$Ba^{++} + SO_4^{=} = \underline{BaSO_4}$$

The precipitate is very insoluble in water and in dilute acids. It is best precipitated from hot solutions. Barium is determined quantitatively in this way. $BaSO_4$ can be transformed into $BaCO_3$ by boiling with Na_2CO_3 or, better still, by a fusion with solid Na_2CO_3. This is a general method of getting insoluble residues into solution and will be employed later in the analysis of the anions (Part III) and in the discussion of systematic analysis (Part IV).

The oxalate, BaC_2O_4, is more soluble in water than the corresponding calcium and strontium oxalates. It is soluble in hot acetic acid, differing in this respect from CaC_2O_4.

PRELIMINARY EXPERIMENTS

1. Precipitation of Barium Carbonate. Add dilute NH_4OH to 2 ml. of the $Ba(NO_3)_2$ test solution until the odor is distinctly ammoniacal. The slight turbidity is not $Ba(OH)_2$ but is due to small amounts of $BaCO_3$ precipitated by $(NH_4)_2CO_3$; this precipitation invariably contaminates the reagent. Heat the solution to boiling and then add ammonium carbonate, $(NH_4)_2CO_3$, in excess. Write the reaction. Filter off the $BaCO_3$ and dissolve it in hot, dilute acetic acid.

2. Reaction with K_2CrO_4. To the hot acetate solution add a few drops of K_2CrO_4 reagent. What forms? Give the equation. This reaction serves to make a fairly good separation of barium from strontium and calcium.

3. Reaction toward the Sulfate Ion. To 2 ml. of $Ba(NO_3)_2$ test solution add $(NH_4)_2SO_4$ reagent. Describe the result. $BaSO_4$ is practically insoluble in all acids and is formed even in very dilute solutions of barium salts by any soluble sulfate or dilute H_2SO_4.

4. Behavior toward the Oxalate Ion. To a small amount of barium test solution add some ammonium oxalate reagent. Does a precipitate form?

5. Flame Coloration. Dip a clean platinum wire into a test tube containing some barium test solution, or gather up some precipitated $BaCrO_4$ or $BaCO_3$ in a loop in the wire and hold it in the outer portion of a Meker or Bunsen burner flame. The flame should show flashes of green. If a non-volatile coating of oxide forms, dip the wire once into dilute HCl and again touch it to the flame.

STRONTIUM, Sr^{++}

Strontium, like barium and calcium, is a divalent element. The reactions of the strontium are much like those of the other two alkaline elements. The carbonate, $SrCO_3$, is readily precipitated by the group reagent, $(NH_4)_2CO_3$. The chromate is much more soluble than $BaCrO_4$. Strontium sulfate, though more soluble than barium sulfate, is precipitated by dilute H_2SO_4 and soluble sulfates; strontium is separated from calcium by virtue of the smaller solubility of $SrSO_4$. The solubility of the chromate as well as that of the oxalate is intermediate between the corresponding salts of barium and calcium.

PRELIMINARY EXPERIMENTS

1. Precipitation of Strontium Carbonate. Add dilute NH_4OH to 2 ml. of the $Sr(NO_3)_2$ test solution, heat to boiling and then add $(NH_4)_2CO_3$ reagent. Write the reaction. $SrCO_3$ is about as insoluble in water and ammonium salts as $BaCO_3$.

2. Behavior toward K_2CrO_4. Filter off and dissolve the $SrCO_3$ in hot, dilute acetic acid. Add a few drops of K_2CrO_4 reagent to the filtrate. Note the result. Only when the amount of strontium ion is considerable will a precipitate of $SrCrO_4$ form.

3. Behavior toward Sulfate Ion. To 2 ml. of $Sr(NO_3)_2$ add some $(NH_4)_2SO_4$ reagent and warm. $SrSO_4$ will be precipitated after standing a few minutes. It is more soluble in water than $BaSO_4$. Repeat the experiment, using a saturated solution of $CaSO_4$ as precipitating agent. Does $SrSO_4$ precipitate? Compare these results with those under calcium below.

4. Behavior toward the Oxalate Ion. Add some $(NH_4)_2C_2O_4$ reagent to some strontium test solution. Note the result. Stron-

tium oxalate, though less soluble than the barium salt, will probably not precipitate.

5. Flame Coloration. Strontium salts when volatilized in a hot flame color the flame red. Try the flame test, using precipitated $SrCO_3$ held in the loop of a platinum wire.

CALCIUM, Ca^{++}

This alkaline earth element is very abundant and of considerable technical importance. It occurs widely as limestone and marble in the form of $CaCO_3$ and finds many uses as the oxide and in other forms.

A glance at the solubility tables (pages 206 and 332) will reveal the relative solubility of the carbonate, chromate, sulfate and oxalate. Calcium is precipitated along with barium and strontium as $CaCO_3$. It is isolated from the group filtrate in the form of the oxalate, CaC_2O_4.

PRELIMINARY EXPERIMENTS

1. Precipitation of Calcium Carbonate. Render 2 ml. of $Ca(NO_3)_2$ test solution ammoniacal with dilute NH_4OH and then add $(NH_4)_2CO_3$ reagent. Write the ionic equation for the reaction.

2. Behavior toward K_2CrO_4. Filter off the precipitated $CaCO_3$ and dissolve it with hot, dilute $HC_2H_3O_2$. Add some K_2CrO_4 to the acetate solution and verify the fact that $CaCrO_4$ is too soluble to be formed.

3. Behavior toward Sulfate Ion. Add dilute $(NH_4)_2SO_4$ to a few milliliters of test solution. Does $CaSO_4$ readily precipitate?

Add a few milliliters of saturated solution of $CaSO_4$ to another portion of the test solution. In which case does more precipitate form?

To a mixture of $Ca(NO_3)_2$ and $Sr(NO_3)_2$ add saturated $CaSO_4$ solution. Show by flame tests that the precipitate formed is $SrSO_4$.

4. Behavior toward the Oxalate Ion. Treat 2 ml. of calcium test solution with $(NH_4)_2C_2O_4$ reagent. Write the reaction. This is the most characteristic reaction of calcium ion and is the test for calcium. Calcium is determined quantitatively as well by precipitation as CaC_2O_4.

Try the solubility of CaC_2O_4 in $HC_2H_3O_2$. Does it dissolve? Will dilute HCl dissolve it? Explain the results.

5. Flame Coloration. Study the flame color of calcium by volatilizing salts of calcium in a hot Bunsen or Meker flame. The color is a yellowish red.

REVIEW EXERCISES — SET 14

1. Why are the members of this group precipitated as carbonates rather than as sulfates, chromates or oxalates? Group together the reactions occurring during the group precipitation.

2. How do Ba^{++}, Sr^{++} and Ca^{++} ions behave toward K_2CrO_4? Explain how a separation might here be made.

3. Explain the color change when a solution of K_2CrO_4 is acidified or when a dichromate solution is made alkaline.

4. Will $(NH_4)_2SO_4$ precipitate $CaSO_4$ equally as well as it will precipitate $SrSO_4$? Will a saturated $CaSO_4$ solution form a precipitate of $SrSO_4$ as readily as it will form a precipitate of $CaSO_4$?

5. Given a solution which contains equal amounts of Sr^{++} and Ca^{++} ions, which reagent would you add, $(NH_4)_2SO_4$ or saturated $CaSO_4$, in order to precipitate $SrSO_4$ in preference to $CaSO_4$? Explain what is meant by fractional precipitation.

6. Calculate the ratio of Ca^{++} ions to Ba^{++} ions in a mixed solution at the time when both $CaSO_4$ and $BaSO_4$ are being precipitated.

7. Explain why HCl will dissolve CaC_2O_4, and $HC_2H_3O_2$ will not dissolve it.

8. Using equilibrium relationships, show how Mg^{++} ion is retained in solution during the precipitation of this group.

9. How does the acidification of the K_2CrO_4 reagent increase the solubility of $SrCrO_4$?

10. The Ca^{++} test reagent contains 10 milligrams of this ion per milliliter. From the data in Table XII calculate the $CO_3^{=}$ concentration required just to saturate such a solution with respect to Ca^{++} and $CO_3^{=}$ ions.

Outline of the Method of Analysis of This Group

From an inspection of Table XII, which gives the solubility of the carbonates, chromates, sulfates and oxalates of the members of this group, it can be seen that the carbonates are uniformly the least soluble, and consequently these cations are first precipitated as carbonates.

In the group precipitation, NH_4Cl is added to the solution along with the ammoniacal $(NH_4)_2CO_3$ in order to prevent the precipitation of magnesium both as $Mg(OH)_2$ and as $MgCO_3$. $Mg(OH)_2$ cannot precipitate because, by common-ion effect, the high concentration of NH_4^+ reduces the OH^- ion concentration to such an extent that the $K_{s.p.}$ of $Mg(OH)_2$ is not exceeded. $MgCO_3$ cannot

precipitate because the excess of NH_4^+ ion lowers the concentration of the $CO_3^=$ ion, by virtue of the formation of HCO_3^- ions, to such an extent that the relatively large value of the $K_{s.p.}$ of $MgCO_3$ is not reached. The presence of NH_4OH in the ammonium carbonate reagent, on the other hand, prevents the hydrolysis of $(NH_4)_2CO_3$ from going too far to completion, and thus not lowering the $CO_3^=$ ion concentration to such an amount that the three alkaline earth carbonates of this group cannot fail to be precipitated.

$BaCO_3$, $SrCO_3$ and $CaCO_3$ are soluble in acids as weak as acetic acid.

TABLE XII

SOLUBILITIES OF ALKALINE EARTH SALTS

Milligrams per 100 ml. of Water

	Carbonate	Chromate	Sulfate	Oxalate
Barium	2.3	0.38	0.23	8.6
Strontium	1.1	120.0	11.0	4.6
Calcium	1.3	400.0	200.0	0.56

Table XII further suggests that the relatively small solubility of $BaCrO_4$ offers the means of separating barium from strontium and calcium. The experiments have shown that $BaCrO_4$ is precipitated from an acetic acid solution whereas $SrCrO_4$ is not. The function of the acetic acid is to convert a certain portion of the $CrO_4^=$ into $Cr_2O_7^=$, thus lowering the chromate-ion concentration so that $SrCrO_4$ is not precipitated. (See under "Chromium," page 193.)

A special case of fractional precipitation is encountered in this group in the partial separation of strontium from calcium by means of $(NH_4)_2SO_4$. The solubility product constant of $SrSO_4$ is 3.6×10^{-7} and that of $CaSO_4$ 2.2×10^{-4} mole per liter. $SrSO_4$ therefore will precipitate before $CaSO_4$ when $SO_4^=$ ions are added to a solution containing both Sr^{++} and Ca^{++} ions. $CaSO_4$ will begin to precipitate along with $SrSO_4$ when the concentrations of Sr^{++} and Ca^{++} remaining in solution bear a ratio to each other proportional to the ratio of their respective solubility product constants. The ratio is 1:610. This means that a precipitate of pure strontium sulfate will form until for every strontium ion remaining there will

be 610 calcium ions. After that both $SrSO_4$ and $CaSO_4$ will precipitate together. The solution can then be regarded as consisting of a saturated solution of both $SrSO_4$ and $CaSO_4$.

DIAGRAMMATIC SCHEME — GROUP IV

Solution:		*Precipitate:*		*Precipitate:*					
Ba^{++}		$BaCO_3$		$BaCrO_4$	Dissolved in HCl, boiled; flame test— green flame proves Ba.				
Sr^{++}	Concentrated to 25 ml. NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ added. Filtered.	$SrCO_3$	Dissolved in warm dilute acetic acid; $NaC_2H_3O_2$ and K_2CrO_4 added. Filtered.	*Filtrate:* Sr^{++}	NaOH, Na_2CO_3 added.	*Precipitate:* $SrCO_3$	Dissolved in acetic acid; small portion tested with $CaSO_4$ solution. If $SrSO_4$ formed $(NH_4)_2SO_4$ added to remaining portion.	*Precipitate:* $SrSO_4$	Flame test — deep red proves Sr.
Ca^{++}		$CaCO_3$		Ca^{++}		$CaCO_3$		*Filtrate:* Ca^{++}	Added $(NH_4)_2C_2O_4$ — white precipitate; flame test — yellowish red proves Ca.

PRACTICE ANALYSIS OF A MIXTURE CONTAINING BARIUM, STRONTIUM AND CALCIUM IONS

Group Precipitation. To a mixture containing 5 ml. each of Ba^{++}, Sr^{++} and Ca^{++} test solution add 10 ml. of water, make slightly ammoniacal with dilute NH_4OH and heat almost to boiling. Then add, slowly with stirring, the group precipitating reagent, ammonium carbonate, $(NH_4)_2CO_3$ until the precipitation appears complete. The precipitate consists of $BaCO_3$, $SrCO_3$ and $CaCO_3$.

After the carbonates have settled, filter them off, washing the residue with hot water. Pour several 3-ml. portions of hot, dilute acetic acid over the precipitate on the filter paper, thus dissolving the carbonates.

Separation and Identification of Barium. Dilute the filtrate containing the acetic acid solution of the dissolved carbonates to 50 ml., heat to boiling, add 10 ml. of $NaC_2H_3O_2$ reagent and then K_2CrO_4 reagent until the solution turns yellow. This shows that an excess of the precipitating reagent has been added. The yellow precipitate is $BaCrO_4$. Allow this to settle and decant off the solution, passing it through a filter. This solution contains the Sr^{++} and Ca^{++} ions. Finally transfer the $BaCrO_4$ to the filter and wash with hot water until the filtrate no longer runs through yellow. Under the conditions of the separation, the precipitate should consist solely of $BaCrO_4$ and no $SrCrO_4$ should have formed.

The identity of the barium chromate should be confirmed by the flame test. Dissolve the precipitate on the filter with HCl and boil the resulting filtrate until the chromate ion is reduced to the green chromic ion. Test for barium by dipping a platinum wire into the solution and then holding it in the outer top edge of a hot Meker or similar burner flame. If a green-colored flame is not produced after several trials, dip the wire into the solution, then into a little concentrated HCl and finally hold in the hottest part of the flame.

Reprecipitation of Strontium and Calcium. In order to get rid of the excess of chromate ions, take the filtrate from the $BaCrO_4$ separation, make it alkaline with NaOH, heat and add Na_2CO_3 reagent until precipitation of $SrCO_3$ and $CaCO_3$ is complete.

Filter off the $SrCO_3$ and $CaCO_3$ and wash with warm water until the filtrate no longer comes through yellow. Discard this filtrate, then dissolve the residue in hot, dilute acetic acid and dilute the filtrate to 50 ml. with water.

Separation and Identification of Strontium. In the analysis of an unknown sample, a preliminary test for strontium is made at this point by adding saturated $CaSO_4$ to a small portion of the solution. This preliminary test may be omitted in the present procedure and the separation of strontium made directly.

To the acetic acid solution obtained in the reprecipitation of the carbonates, add 5 ml. of $(NH_4)_2SO_4$ reagent, warm and allow to stand for several minutes. Filter off the precipitate.

The precipitate may not be pure $SrSO_4$. Any barium which failed to precipitate as $BaCrO_4$ may now have precipitated as $BaSO_4$. Furthermore, some $CaSO_4$ may have precipitated.

This separation of strontium is therefore not sharp. The precipitate should be identified as consisting mainly of $SrSO_4$ by a flame test.

Make a flame test for strontium by moistening the residue with a few drops of HCl and then taking up some of the solid in the loop of a platinum wire and holding it in a hot flame. The deep red color shows the presence of strontium.

Identification of Calcium. The filtrate from the $SrSO_4$ removal contains the calcium. To precipitate this, add ammonium oxalate, $(NH_4)_2C_2O_4$ until CaC_2O_4 no longer precipitates. Filter off the precipitate and wash with dilute acetic acid. Confirm the presence of calcium by the flame test. The flame will have a yellowish red color in the presence of calcium.

THE SOLUBLE CATION GROUP — GROUP V

MAGNESIUM, Mg^{++}	**SODIUM, Na^+**
POTASSIUM, K^+	**AMMONIUM, NH_4^+**

In a systematic separation of the cations into groups by the use of HCl, H_2S, $(NH_4)_2S$ and $(NH_4)_2CO_3$ the ions of this group fail to precipitate as chlorides, sulfides, hydroxides or carbonates. They therefore remain in solution as ions and must be detected by separate, individual tests. Though the carbonate and hydroxide of magnesium are relatively insoluble, the use of NH_4Cl, supplied in the precipitation of Groups III and IV, prevents the formation and removal of $Mg(OH)_2$ and $MgCO_3$; hence Mg^{++} ion will remain in solution and is here included as a member of this group. The alkali elements, potassium and sodium, properly belong to this group; in more elaborate schemes of analysis the other three alkali metals, lithium, rubidium and cesium are also detected here; for this reason this group is sometimes referred to as the "alkali metal group." The ammonium ion is included here for discussion, study and experimentation, because it resembles potassium in its tendency to form certain characteristic insoluble salts similar to those of potassium.

The ions of this group are identified by separate, specific tests. Since ammonium compounds have been added during the systematic separation of preceding groups, the test for this radical is always made on a separate portion of the original sample.

MAGNESIUM, Mg^{++}

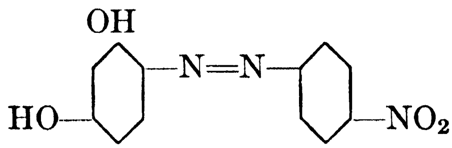
Most of the salts of magnesium are soluble in water. The hydroxide, carbonate, phosphate and ammonium phosphate, however, are not. $Mg(OH)_2$ and $MgCO_3$ cannot form in the presence of an excess of NH_4Cl, hence magnesium is prevented from precipitating in the preceding groups. The sulfide is too readily hydrolyzed to be precipitated.

From an analytical standpoint the most important salt of magnesium is magnesium ammonium phosphate, $MgNH_4PO_4$, a white finely crystalline precipitate, which forms:

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} = \underline{MgNH_4PO_4}$$

in an ammoniacal solution in the presence of an ammonium salt such as NH_4Cl. The reaction is used as the basis for the detection as well as the quantitative determination of magnesium. Conversely, the same reaction may be utilized in the detection and determination of phosphates, and an analogous reaction with the $AsO_4^{\equiv}$ ion serves as a method for the detection of arsenic.

A sensitive test for magnesium is the formation of a "lake" or adsorption complex with the dye, para-nitrobenzene-azo-resorcinol. The organic compound has the structural form shown by the formula:



In an alkaline solution, the Mg^{++} forms $Mg(OH)_2$ which then adsorbs the dyestuff, producing a deep blue color.

PRELIMINARY EXPERIMENTS

1. Non-Precipitation of $Mg(OH)_2$ and $MgCO_3$ in Ammonium Chloride Solutions. To about 2 ml. of $Mg(NO_3)_2$ test solution add a few milliliters of NH_4Cl solution and then add NH_4OH. Repeat the experiment, omitting the NH_4Cl. In which solution does precipitation occur? Explain the action of NH_4Cl on the basis of ionic equilibrium and solubility product relationships.

Repeat the experiment, using $(NH_4)_2CO_3$ as the precipitating agent; add NH_4Cl in one case and omit it in the other. The white precipitate in the one case is a basic carbonate of magnesium.

2. Precipitation of Magnesium Ammonium Phosphate. To a few milliliters of $Mg(NO_3)_2$ test solution add a few crystals of NH_4Cl and then NH_4OH until the solution is ammoniacal. Then add Na_2HPO_4 reagent. Write the reaction. Why was NH_4Cl added first? If precipitation does not take place at once, allow the test to stand for some minutes or rub the inside of the test tube with a stirring rod to start precipitation.

3. Para-Nitrobenzene-Azo-Resorcinol Test. To 1 ml. of neutral or slightly acid test solution add an equal volume of the reagent. What color change takes place? What type of product is formed? In case a yellow color results, repeat the experiment with a less acid test solution.

AMMONIUM, NH_4^+

The ammonium ion resembles potassium in many of its reactions. Its insoluble salts, such as the acid tartrate, chloroplatinate and cobaltinitrite, have about the same solubility as the corresponding salts of potassium. For this reason ammonium salts must be removed from solutions which are being used for potassium. For the reason that ammonium salts have been introduced as group reagents in preceding groups, the test for NH_4^+ must always be made on a portion of the original sample.

The test most commonly used to detect the presence of ammonium salts is the action of NaOH. This strongly ionized base will liberate NH_3 from solutions containing the NH_4^+ ion, and the presence of NH_3 can be shown by its ability to turn moist litmus paper blue.

The liberation of NH_3 from solutions of ammonium compounds by NaOH is explained as follows: The action of the strong base on the ammonium salt present is first to form NH_4OH, because this compound is a weakly ionized substance:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

Ammonium hydroxide is in equilibrium with NH_3 and H_2O, since it is produced by the reaction of ammonia with water:

$$NH_4OH \rightleftharpoons NH_3 + H_2O$$

Addition of a large excess of OH^- ions from the strong base will repress the ionization of NH_4OH. But the concentration of non-ionized NH_4OH is limited by its equilibrium with NH_3, and to maintain the above constant, NH_3, as gas, is evolved from the

equilibrium mixture. The ammonia reacts with the water on the moist litmus paper, forming the base which gives the blue color.

Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, gives with ammonium salts a yellow precipitate of $(NH_4)_3Co(NO_2)_6$, similar in appearance to that formed by potassium salts.

Chloroplatinic acid, H_2PtCl_6, yields a yellow precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, with solutions containing NH_4^+. In the absence of potassium, which yields a similar precipitate, this reaction is a good test for ammonium salts and constitutes a quantitative method of analysis as well. When ignited, $(NH_4)_2PtCl_6$ leaves a residue of spongy platinum:

$$(NH_4)_2PtCl_6 = \overline{2NH_3} + \overline{2HCl} + \overline{2Cl_2} + \underline{Pt}$$

Tartaric acid, $H_2C_4H_4O_6$, precipitates from concentrated solutions of ammonium salts white crystalline ammonium acid tartrate, $NH_4HC_4H_4O_6$, similar in appearance to that produced by potassium.

When ammonium nitrate is strongly heated, it is decomposed into nitrous oxide and water, and thereby completely volatilized:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

This is the method by which ammonium salts are removed from mixtures which are to be examined for potassium.

PRELIMINARY EXPERIMENTS

1. Test for Ammonium Ion. To a few milliliters of NH_4NO_3 test solution in a small beaker, add 1 ml. of NaOH solution. Stir the mixture. Hold over the solution a piece of moistened red or neutral litmus paper. If no color change occurs or if the odor of NH_3 is not evident, cautiously warm the mixture, again testing the vapors with litmus paper. Explain the action of NaOH, in terms of ionic equilibria and common-ion effect. Write reactions to show why NH_3 is evolved.

2. Decomposition of Ammonium Compounds. Add concentrated HNO_3 to a few milliliters of NH_4Cl or NH_4NO_3 solution, evaporate carefully to dryness in a small evaporating dish and then heat the dish to a dull red heat. Does a residue still remain? Do sodium and potassium salts show the same behavior?

POTASSIUM, K^+

The potassium ion is always monovalent. The oxide, K_2O, is relatively unimportant but the hydroxide, KOH, is an important

reagent. It is formed when the metal reacts with water:

$$2K + 2H_2O = 2K^+ + 2OH^- + H_2$$

A solution of KOH is highly ionized and hence strongly alkaline. The commoner salts of potassium are rather soluble in water. The insoluble salts are the cobaltinitrite, the chloroplatinate, the acid-tartrate and the perchlorate. The precipitation of these salts may be used as tests for potassium, provided the ammonium ion is absent.

When sodium cobaltinitrite is added to a dilute solution containing potassium ion, there is formed a yellow precipitate of potassium-sodium cobaltinitrite, according to the equation:

$$2K^+ + Na^+ + Co(NO_2)_6^{\equiv} = \underline{K_2NaCo(NO_2)_6}$$

If much potassium is present, the compound will have the composition represented by the formula $K_3Co(NO_2)_6$. As already noted, ammonium ion precipitates $(NH_4)_2NaCo(NO_2)_6$; hence, in using this reaction as a test for potassium, ammonium salts must be absent.

Potassium chloroplatinate, K_2PtCl_6, a yellow precipitate, is formed when chloroplatinic acid (a solution of platinum in aqua regia) is added to a strong solution of a potassium salt such as the nitrite. The reaction is:

$$2K^+ + PtCl_6^{=} = \underline{K_2PtCl_6}$$

This is another good test for potassium and is one of the methods used for the quantitative determination of potassium. Since the NH_4^+ ion produces $(NH_4)_2PtCl_6$, similar in color, this test can only be used in the absence of ammonium salts.

A solution of tartaric acid, or of sodium acid tartrate, will precipitate potassium acid tartrate, $KHC_4H_4O_6$, from a neutral solution of a potassium salt.

$$K^+ + HC_4H_4O_6^- = \underline{KHC_4H_4O_6}$$

As with the two other reactions already cited, the presence of NH_4^+ interferes.

Perchloric acid, $HClO_4$, precipitates $KClO_4$ from alcoholic solutions containing K^+ ion. The reaction is used quantitatively for the determination of potassium.

PRELIMINARY EXPERIMENTS

The instructor will specify which of the following reactions should be studied.

1. Reaction with Sodium Cobaltinitrite. To about 1 ml. of the test solution add an equal volume of sodium cobaltinitrite and allow the test to stand for several minutes. Write the equation for the reaction. It should be remembered that the corresponding ammonium salt is also insoluble.

2. Chloroplatinate Test. The reaction with this reagent constitutes a sensitive test for potassium and is one of the methods by which potassium is determined quantitatively. The reagent is expensive; the instructor will specify whether this reaction is to be carried out and will personally dispense the reagent.

Place a few drops of test solution on a watch glass or in a test tube and ask the laboratory instructor to add a drop of the chloroplatinic acid. What forms? Give the equation.

The ammonium ion forms $(NH_4)_2PtCl_6$, similar in appearance to the potassium salt.

3. Reaction with Perchloric Acid. Add to 2 ml. of the test solution of KNO_3 an equal volume of ethyl alcohol, C_2H_5OH, and then add, dropwise, a dilute solution of perchloric acid, $HClO_4$. This reaction will distinguish potassium from sodium. The quantitative determination of potassium can be carried out by this reaction.

4. Precipitation of Potassium Acid Tartrate. Add a few milliliters of tartaric acid solution, $H_2C_4H_4O_6$, or sodium acid tartrate, $NaHC_4H_4O_6$, to 2 ml. of the KNO_3 test solution and shake vigorously. What is the composition of the precipitate formed? See experiment 5 for ammonium.

5. Flame Coloration. Dip a clean platinum wire into KNO_3 test solution contained in a watch glass and hold the wire in the outer part of a Bunsen flame. Note the color of the flame.

Add some $NaNO_3$ to the KNO_3 in the watch glass and repeat the experiment, observing the flame test first without and then with a thick cobalt glass plate. The blue glass absorbs the yellow rays owing to the presence of sodium and transmits only the color of the potassium flame.

SODIUM, Na^+

All of the common salts of sodium are soluble in water. The triple salt which forms with zinc uranyl acetate is the best precipitation test for sodium. The fluosilicate, Na_2SiF_6, and the pyroantimonate, $Na_2H_2Sb_2O_7$, are slightly soluble in water and sometimes

employed as tests for this element. The color of the sodium flame is an intense yellow.

Zinc uranyl acetate forms a pale yellow precipitate with Na^+. The precipitate is sodium zinc uranyl acetate, and has the composition:

$$NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O$$

High concentrations of potassium will produce a similar triple salt. The reagent is a mixture of zinc acetate and uranyl acetate in dilute acetic acid solution.

Fluosilic acid, H_2SiF_6, will precipitate from solutions of sodium salts, in the presence of alcohol, a white gelatinous precipitate of Na_2SiF_6. Potassium must be absent because the similar salt, K_2SiF_6, would be precipitated and NH_4^+ must be absent because in the presence of ammonium salts the reagent decomposes into orthosilic acid, H_4SiO_4, which resembles Na_2SiF_6 in appearance.

Potassium pyroantimonate, $K_2H_2Sb_2O_7$, reacts with sodium salts to precipitate sodium pyroantimonate, $Na_2H_2Sb_2O_7$, in neutral or weakly basic solutions.

PRELIMINARY EXPERIMENTS

1. Zinc Uranyl Acetate Test. To 2 drops of Na^+ test solution in a test tube add a large excess (about 10 drops) of the acetate reagent. Shake the tube and after several minutes note the presence of a precipitate. Give its formula.

2. Flame Test. Thoroughly clean a platinum wire by alternately dipping it in concentrated HCl and then touching it to the flame of a Bunsen burner. Study the color of the flame produced when sodium salts are volatilized. Try several different salts of sodium. Compare the color with that produced by ammonium compounds. Note that appreciable amounts of sodium give an intense, persistent dandelion-yellow flame whereas the traces of sodium present in ammonium salts and most other reagents give only a feeble, dull yellow flame of short duration.

REVIEW EXERCISES — SET 15

1. $Mg(OH)_2$ is quite insoluble. It forms when Mg ions react with bases such as NH_4OH. Explain, on the basis of the solubility product principle, why $Mg(OH)_2$ is not precipitated in Group III, where NH_4OH in the presence of NH_4Cl is used.

2. $MgCO_3$ can be precipitated by $(NH_4)_2CO_3$. Explain why it is not precipitated in Group IV along with $BaCO_3$, $CaCO_3$ and $SrCO_3$.

3. Give the reaction which represents a test for magnesium.

4. Name and give formulas of four insoluble salts of potassium and two of sodium.

5. Can sodium be separated from potassium with chloroplatinic acid?

6. What is a good precipitation test for potassium? Write the reaction. Will this test work if NH_4^+ ions are also present?

7. Are potassium salts more volatile in the flame than sodium salts? Why use a blue (cobalt) glass?

8. How do ammonium salts behave with H_2PtCl_6, $Na_3Co(NO_2)_6$ and $H_2C_4H_4O_6$? Can any of these reagents be used for tests if potassium ion is present?

9. Explain, on the basis of the Law of Chemical Equilibrium, how a strong base will displace a weaker base from its salts.

10 Calculate the approximate OH^- concentration for a molar solution of NH_4OH to which a gram-mole of NH_4Cl has been added. (NH_4Cl is ionized 84 per cent.)

Practice Analysis of a Mixture Containing Magnesium, Ammonium, Potassium and Sodium Ions

Make up a mixture of these ions by mixing 5 ml. of each of the test solutions of these four cations. Use separate portions for the individual tests as outlined in the accompanying procedures.

Identification of Magnesium. To about 5 ml. of the test mixture add a few crystals of NH_4Cl, made ammoniacal with NH_4OH, and then add 2 ml. of disodium hydrogen phosphate, Na_2HPO_4. The reaction:

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} = \underline{MgNH_4PO_4}$$

forms the white crystalline salt of magnesium ammonium phosphate, usually after standing for some time.

To confirm this apply the test with para-nitrobenzene-azo-resorcinol: To 1 ml. of the test mixture, which should be neutral, add 1 ml. of the alkaline organic test reagent. The deep blue precipitate (a lake) is due to the adsorption of the dye on the precipitated hydroxide.

Identification of the Ammonium Ion. To another portion of the test mixture, in a small beaker, add a solution of NaOH. Moisten a strip of red or neutral litmus paper to the bottom of a watch glass and place this over the beaker. Then warm the mixture, being careful that no drops of the solution come into contact with the

test paper. Ammonia, NH_3, will be displaced from the solution through the action of the strong base and, on reacting with the moisture on the test paper, will render it blue.

Identification of Potassium. In order to apply the precipitation tests for potassium the ammonium ion must be removed. Proceed as follows: Place about 5 ml. of the solution in a large evaporating dish or casserole, add an equal volume of concentrated HNO_3 and begin the evaporation of the solution. (While this is in progress, the identification of sodium and ammonium can be carried out.) When the solution is reduced to a small volume transfer it to a smaller evaporating dish and carefully apply the heat to avoid spattering as the mixture becomes dry. Then ignite below a dull, red heat until fumes are no longer given off. This treatment volatilizes the ammonium salts:

$$NH_4NO_3 = 2H_2O + N_2O$$

Allow the residue to cool.

Remove some of the residue to a test tube, dissolve in a few milliliters of water, adding a drop or two of acetic acid. Filter if necessary. To a portion of this filtrate add about 1 ml. of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, warm and allow to stand for several minutes. The yellow precipitate is potassium cobaltinitrite, $K_2NaCo(NO_2)_6$.

If chloroplatinic acid is available, the test with this reagent is carried out as follows: Remove to a watch glass a drop or two of the solution from which ammonium salts have been removed and ask the instructor to add a drop of H_2PtCl_6. The yellow precipitate is potassium chloroplatinate, K_2PtCl_6.

To apply the flame test, a bit of the ignited residue may be taken up in the loop of a platinum wire, held in the outer part of a Bunsen flame; the flame must be viewed through a thick blue (cobalt) glass. The violet color transmitted through the glass, which screens out the yellow of the sodium, is characteristic of potassium.

Identification of Sodium. To a drop or two of the test mixture, add 8 to 12 drops of zinc uranyl acetate reagent. In the course of five minutes or so, the triple salt, $NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3(UO_2)(C_2H_3O_2)_2 \cdot 6H_2O$, sodium zinc uranyl acetate will form as a pale yellow precipitate.

The flame test for sodium as conducted here will give a bright, intense yellow color which lasts for some time.

TABLE XIII

Behavior of Cations toward Certain Reagents

Cation	Dilute HCl	H_2S (HCl)	$(NH_4)_2S$	$(NH_4)_2CO_3$		NH_4OH		NaOH	
				Equiv. Amount	Excess	Equiv. Amount	Excess	Equiv. Amount	Excess
Ag^+	$AgCl$ white	Ag_2S black	Ag_2S black	Ag_2CO_3 white	sol. $Ag(NH_3)_2^+$	Ag_2O brown	sol. $Ag(NH_3)_2^+$	Ag_2O brown	insol.
Hg_2^{++}	Hg_2Cl_2 white	Hg_2S black	Hg_2S black	$HgNH_2Cl+Hg$ white black	insol.	$HgNH_2Cl+Hg$ white black	insol.	$Hg_2(OH)_2$ white	insol.
Pb^{++}	$PbCl_2$ white	PbS black	PbS black	$PbCO_3 \cdot Pb(OH)_2$ white	insol.	$Pb(OH)_2$ white	insol.	$Pb(OH)_2$ white	sol. Na_2PbO_2
Hg^{++}	......	HgS black	HgS black	$HgCO_3(HgO)_3$ brown	insol.	$HgNH_2Cl$ white	insol.	HgO yellow	insol.
Bi^{+++}	......	Bi_2S_3 black	Bi_2S_3 black	$Bi(OH)CO_3$ white	insol.	$Bi(OH)_3$ white	insol.	$Bi(OH)_3$ white	insol.
Cu^{++}	......	CuS black	CuS black	$CuCO_3$ blue	sol. $Cu(NH_3)_4^{++}$ deep blue	$Cu(OH)_2$ blue	sol. $Cu(NH_3)_4^{++}$ deep blue	$Cu(OH)_2$ blue	insol.
Cd^{++}	......	CdS yellow	CdS yellow	$CdCO_3$ white	sol. $Cd(NH_3)_4^{++}$ colorless	$Cd(OH)_2$ white	sol. $Cd(NH_3)_4^{++}$ colorless	$Cd(OH)_2$ white	insol.
As^{+++} AsO_2^-	......	As_2S_3 yellow	As_2S_3 sol. in excess	.....	..	......	.....	......	......
Sb^{+++}	......	Sb_2S_3 orange	Sb_2S_3 sol. in excess	$Sb(OH)_3$ white	insol.	$Sb(OH)_3$ white	insol.	$Sb(OH)_3$ white	sol. Na_3SbO_3
Sn^{++}	......	SnS brown	SnS sol. in excess	$Sn(OH)_2$ white	insol.	$Sn(OH)_2$ white	insol.	$Sn(OH)_2$ white	sol. Na_2SnO_2
Sn^{++++}	......	SnS_2 yellow	SnS_2 sol. in excess	$Sn(OH)_4$ white	insol.	$Sn(OH)_4$ white	insol.	$Sn(OH)_4$ white	sol. Na_2SnO_3

Ni^{++}	......	...	NiS black	$Ni_5(OH)_6(CO_3)_2$ green	sol. $Ni(NH_3)_4^{++}$ blue	$Ni(OH)NO_3$ green	sol. $Ni(NH_3)_4^{++}$ blue	$Ni(OH)_2$ green	insol.
Co^{++}	......	......	CoS black	$Co_8O_5(CO_3)_3$ red or pink	sol. $Co(NH_3)_4^{++}$ pink to brown	same as for NaOH but incomplete	sol. $Co(NH_3)_4^{++}$ pink	basic salt, varied color	insol.
Fe^{++}	...	......	FeS black	$FeCO_3$ white	sol.	$Fe(OH)_2$ white to green to brown	insol.	$Fe(OH)_2$ white to green to brown	insol.
Fe^{+++}	......	......	Fe_2S_3 black	$Fe(OH)_3$ red-brown	insol.	$Fe(OH)_3$ red-brown	insol.	$Fe(OH)_3$ red-brown	insol.
Mn^{++}	......	......	MnS pink to brown $MnO(OH)_2$	$MnCO_3$ white	insol.	$Mn(OH)_2$ white to brown	insol.	$Mn(OH)_2$ white to brown	insol.
Al^{+++}	......	......	Hydrolyzed to $Al(OH)_3$ white	$Al(OH)_3$ white	insol.	$Al(OH)_3$ white	insol.	$Al(OH)_3$ white	sol. $NaAlO_2$
Cr^{+++}	.	...	Hydrolyzed to $Cr(OH)_3$ green	$Cr(OH)_3$ green	insol.	$Cr(OH)_3$ green	insol.	$Cr(OH)_3$ green	sol. Na_3CrO_3
Zn^{++}	......	......	ZnS white	$ZnCO_3$ white	sol. $Zn(NH_3)_4^{++}$	$Zn(OH)_2$ white	sol. $Zn(NH_3)_4^{++}$	$Zn(OH)_2$ white	sol. Na_2ZnO_2
Ba^{++}	....	......	......	$BaCO_3$ white	insol.	......	....	$Ba(OH)_2$	......
Sr^{++}	......	......	......	$SrCO_3$ white	insol.	.	......	$Sr(OH)_2$	......
Ca^{++}	......	......	......	$CaCO_3$ white	insol.	......	......	$Ca(OH)_2$	......
Mg^{++}	......	......	......	basic $MgCO_3.Mg(OH)_2$ white	sol. in presence of NH_4Cl	$Mg(OH)_2$ white	sol. in presence of NH_4Cl	$Mg(OH)_2$ white	......
K^+	......	......	......	....	......	......	......	......	....
Na^+	......	......	......	....	......	......	.....	...	......
NH_4^+	......	......	......	......	......		......	......	......

PART III

THE REACTIONS OF THE ANIONS

The anions or acid radicals studied in this course are derived primarily from relatively few elements. The acid-forming elements which give rise to the most important and commoner acids are the following:

FLUORINE	**CARBON**
CHLORINE	**BORON**
BROMINE	**PHOSPHORUS**
IODINE	**ARSENIC**
SULFUR	**CHROMIUM**
NITROGEN	**SILICON**

From the acids or salts of these elements, by ionization, are produced the anions, whose study is undertaken here. They are:

FLUORIDE, F^-
CHLORIDE, Cl^-, and **CHLORATE,** ClO_3^-
BROMIDE, Br^-
IODIDE, I^-
SULFIDE, $S^=$, **SULFITE,** $SO_3^=$, **SULFATE,** $SO_4^=$, **THIOSULFATE,** $S_2O_3^=$, and **THIOCYANATE,** CNS^-
NITRITE, NO_2^-, and **NITRATE,** NO_3^-
CARBONATE, $CO_3^=$, **OXALATE,** $C_2O_4^=$, **TARTRATE,** $C_4H_4O_6^=$, **ACETATE,** $C_2H_4O_2^-$, **CYANIDE,** CN^-, **FERROCYANIDE,** $Fe(CN)_6^{==}$, and **FERRICYANIDE,** $Fe(CN)_6^{\equiv}$
BORATE, BO_2^-, $BO_3^{\equiv}$, $B_4O_7^=$
PHOSPHATE, $PO_4^{\equiv}$
ARSENATE, $AsO_4^{\equiv}$, and **ARSENITE,** $AsO_2^-(AsO_8^{\equiv})$
CHROMATE, $CrO_4^=$ or $Cr_2O_7^=$
SILICATE, $SiO_3^=$

THE ANALYTICAL GROUPING OF THE ANIONS

The method by which the anions are placed into several groups, subsequently subdivided and finally detected individually follows the general principle of that of the cation scheme. The anion

scheme used here is that originally proposed by Dobbins and Ljung of the University of North Carolina and with certain alterations has been found to give good results when used by students. In this procedure the solution of the ions is kept rather strongly alkaline with NaOH in order to minimize the destructive effects of oxidation-reduction reactions. The group reagents are $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$, thus dividing the anions into four precipitated groups and a soluble group. The group precipitations are here outlined.

1. If $Ca(NO_3)_2$ reagent is added to a mixture of all anions there will be precipitated calcium carbonate, $CaCO_3$, calcium oxalate, CaC_2O_4, calcium fluoride, CaF_2, calcium metaborate, $Ca(BO_2)_2$, calcium sulfite, $CaSO_3$, calcium arsenite, $Ca(AsO_2)_2$, calcium arsenate, $Ca_3(AsO_4)_2$, calcium phosphate, $Ca_3(PO_4)_2$, calcium tartrate, $CaC_4H_4O_6$, and calcium silicate, $CaSiO_3$. It may happen, also, that some $Ca(OH)_2$ precipitates. This group of calcium salts is Group I. The supernatant liquid or filtrate will contain all other anions of which the mixture is composed.

2. If to the filtrate is next added $Ba(NO_3)_2$ reagent, insoluble barium sulfate, $BaSO_4$, and barium chromate, $BaCrO_4$, will form. This then is Group II.

3. $Zn(NO_3)_2$ is the reagent for Group III and will precipitate zinc sulfide, ZnS, zinc cyanide, $Zn(CN)_2$, zinc ferrocyanide, $Zn_2Fe(CN)_6$, and zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$.

4. Having removed, successively, the insoluble calcium, barium and zinc salts, if now $AgNO_3$ reagent is added, there will be precipitated silver thiosulfate, $Ag_2S_2O_3$, silver thiocyanate, $AgCNS$, silver iodide, AgI, silver bromide, $AgBr$, and silver chloride, $AgCl$. This is Group IV.

5. There remain, unprecipitated by the group reagents, the chlorate, ClO_3^-, the acetate, $C_2H_3O_2^-$, the nitrite, NO_2^-, and the nitrate, NO_3^-. These may be considered Group V.

This grouping of the anions is shown diagrammatically on the following page.

The properties, reactions and tests for the anions are described in the following sections. In the systematic analysis of mixtures the test for nitrates must be made on a separate portion of the original mixture, because the nitrate ion is introduced through the addition of the group reagents.

DIAGRAMMATIC GROUPING OF THE ANIONS

$CO_3^=$		$CaCO_3$							
$C_2O_4^=$		CaC_2O_4							
F^-		CaF_2							
BO_2^-		$Ca(BO_2)_2$							
$SO_3^=$		$CaSO_3$	Group I						
AsO_2^-		$Ca(AsO_2)_2$							
$AsO_4^{\equiv}$		$Ca_3(AsO_4)_2$							
$PO_4^{\equiv}$		$Ca_3(PO_4)_2$							
$C_4H_4O_6^=$		$CaC_4H_4O_6$							
$SiO_3^=$		$CaSiO_3$							
$SO_4^=$		$SO_4^=$		$BaSO_4$	Group II				
$CrO_4^=$	NaOH	$CrO_4^=$		$BaCrO_4$					
$S^=$	$Ca(NO_3)_2$	$S^=$		$S^=$		ZnS			
CN^-		CN^-		CN^-		$Zn(CN)_2$	Group III		
$Fe(CN)_6^{----}$		$Fe(CN)_6^{----}$		$Fe(CN)_6^{----}$		$Zn_2Fe(CN)_6$			
$Fe(CN)_6^{\equiv}$		$Fe(CN)_6^{\equiv}$		$Fe(CN)_6^{\equiv}$		$Zn_3[Fe(CN)_6]_2$			
$S_2O_3^=$		$S_2O_3^=$		$S_2O_3^=$		$S_2O_3^=$		Ag_2S	
CNS^-		CNS^-	$Ba(NO_3)_2$	CNS^-		CNS^-		$AgCNS$	
I^-		I^-		I^-	$Zn(NO_3)_2$	I^-		$AgCl$	Group IV
Br^-		Br^-		Br^-		Br^-		$AgBr$	
Cl^-		Cl^-		Cl^-		Cl^-	$AgNO_3$	AgI	
ClO_3^-		ClO_3^-		ClO_3^-		ClO_3^-		ClO_3^-	
$C_2H_3O_2^-$		$C_2H_3O_2^-$		$C_2H_3O_2$		$C_2H_3O_2^-$		$C_2H_3O_2^-$	Group V
NO_2^-		NO_2^-		NO_2^-		NO_2^-		NO_2^-	
NO_3^-		NO_3^-		NO_3^-		NO_3^-		NO_3^-	

THE CALCIUM NITRATE GROUP — GROUP I

CARBONATE, $CO_3^{=}$	**ARSENITE, AsO_2^-**
OXALATE, $C_2O_4^{=}$	**ARSENATE, $AsO_4^{\equiv}$**
FLUORIDE, F^-	**PHOSPHATE, $PO_4^{\equiv}$**
METABORATE, BO_2^-	**TARTRATE, $C_4H_4O_6^{=}$**
SULFITE, $SO_3^{=}$	**(SILICATE, $SiO_3^{=}$)**

The anions of this group are precipitated by $Ca(NO_3)_2$; the calcium salts of all other ions are sufficiently soluble to prevent their precipitation here. In a systematic analysis of a solution for the detection of anions, the addition of the group reagent, 1 *M* $Ca(NO_3)_2$ to the solution, which has been made strongly alkaline with 4 *M* NaOH, will result in the precipitation of $CaCO_3$, CaC_2O_4, CaF_2, $Ca(BO_2)_2$, $Ca(AsO_2)_2$, $Ca_3(AsO_4)_2$, $Ca_3(PO_4)_2$, $CaC_4H_4O_6$ and $CaSiO_3$, as well as possibly some $Ca(OH)_2$. The group precipitate, after filtering and thorough washing, is then treated with dilute $HC_2H_3O_2$, which dissolves all except the CaC_2O_4 and CaF_2. Further details of separation and the distinctive reactions which constitute the identification tests are revealed in the following preliminary experiments and practice analysis.

The inclusion of silicates in mixtures of anions for student analysis greatly complicates the scheme of analysis and they are therefore excluded from the systematic scheme. Special provision is, however, made for the detection of this ion in silicate materials. For details see page 319.

CARBONATE, $CO_3^{=}$

When carbon dioxide dissolves in water, carbonic acid is formed, in accordance with the equation:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The amount of H_2CO_3 formed is very small, and the resulting solution very dilute with respect to the acid. Carbonic acid is a weakly ionized acid, dissociating in two stages, viz:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-.$$

and

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}.$$

yielding the bicarbonate and the carbonate ion, respectively.

Alkali carbonates, such as Na_2CO_3, hydrolyze to give an alkaline reaction:

$$CO_3^{=} + H_2O = HCO_3^{-} + OH^{-}$$

Bicarbonates also undergo slight hydrolysis with the formation of H_2CO_3:

$$HCO_3^{-} + H_2O = H_2CO_3 + OH^{-}$$

All the metallic carbonates are insoluble in water, with the exception of ammonium carbonate and the carbonates of the alkali metals. Therefore, when a sample containing soluble or insoluble salts is boiled with Na_2CO_3 (or a solid mixture is fused with Na_2CO_3) transposition will take place, precipitating the metallic ions as insoluble carbonates or, in a few instances, as basic carbonates or hydroxides. If, for example, $BaSO_4$ is boiled or fused with Na_2CO_3, metathesis takes place:

$$\underline{BaSO_4} + Na_2CO_3 = \underline{BaCO_3} + 2Na^{+} + SO_4^{=}$$

transforming the barium sulfate into barium carbonate, leaving in solution $SO_4^{=}$ and Na^{+} ions. This is the basis of the procedure used in systematic anion analysis for freeing the sample of the presence of objectional cations and, at the same time, for getting the sample into solution. The solution thus produced is referred to as the "prepared solution."

The carbonate ion is precipitated, as stated above, by practically all cations. It is important to note that this is especially true of the cations of the group reagents, namely, Ca^{++}, Ba^{++}, Zn^{++} and Ag^{+}, which form the corresponding insoluble carbonates. The reagent of this group, $Ca(NO_3)_2$, precipitates white $CaCO_3$:

$$CO_3^{=} + Ca^{++} = \underline{CaCO_3}$$

The usual test for carbonates depends upon the liberation of CO_2 by the action of an acid and the subsequent reaction of the CO_2 with $Ba(OH)_2$ or $Ca(OH)_2$. When a soluble or insoluble carbonate, such as $CaCO_3$, is treated with an acid, even one as weakly ionized as $HC_2H_3O_2$, carbonic acid is formed:

$$\underline{CaCO_3} + 2H^{+} = H_2CO_3 + Ca^{++}$$

The unstable H_2CO_3 decomposes into carbon dioxide and water:

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

Then, if the gas is exposed to or led into a solution of $Ba(OH)_2$, insoluble $BaCO_3$ forms:

$$CO_2 + H_2O + Ba(OH)_2 = \underline{BaCO_3} + 2H_2O$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Treat 2 ml. of Na_2CO_3 test solution with the $Ca(NO_3)_2$ reagent. What forms? Record the reaction.

2. Test for Carbonate. Decant the supernatant liquid. Hold a drop of $Ba(OH)_2$ in a loop of a platinum wire and place it over the mouth of the test tube containing the $CaCO_3$ precipitated in experiment 1. Then add a few drops of dilute (12.5 per cent) acetic acid. What happens to the $CaCO_3$ and to the drop of $Ba(OH)_2$? Give the equations.

OXALATE, $C_2O_4^{=}$

Oxalates are the salts of oxalic acid. This organic acid is a white solid, crystallizing with two molecules of water, $H_2C_2O_4 \cdot 2H_2O$. It ionizes in two stages, viz:

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$$

and

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{=}$$

It yields acid oxalates and normal oxalates upon reaction with bases. Most of the oxalates are relatively insoluble in water. The relative solubility of calcium, strontium and barium oxalate has already been considered in connection with the separation of calcium in Group IV of the cations.

Calcium oxalate is soluble in strong acids but insoluble in dilute $HC_2H_3O_2$. In this respect it differs, along with CaF_2, from the calcium salts of the other members of this group; this property is used to separate calcium oxalate and calcium fluoride from the other calcium salts of this group.

Oxalic acid and acidified solutions of oxalates are excellent reductants. The reduction of $KMnO_4$ is used as a characteristic test. If $KMnO_4$ is added to an acidified solution of an oxalate, the mixture will be decolorized, owing to the reduction of the pink MnO_4^- ion to colorless Mn^{++}. The reaction in ionic form is:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{=} = 2Mn^{++} + 8H_2O + 10CO_2$$

or, in molecular form:

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + 8H_2O + 10CO_2 + K_2SO_4$$

It must be remembered that many other reducing agents reduce $KMnO_4$ with resultant decolorization of the solution. Particularly will sulfites and arsenites, both members of this group, decolorize $KMnO_4$ and hence in systematic analysis special care must be exercised in the complete removal of these interfering reducing ions.

Since the oxalates of the alkaline earth group (Group IV of the cations), namely CaC_2O_4, SrC_2O_4 and BaC_2O_4, are insoluble in a neutral or alkaline solution, it is important in the systematic detection of the cations that the presence or absence of oxalates be known before beginning the precipitation of Group III of the cations and, if present, they must be removed. The method of removal consists in destroying the oxalate, along with tartrates and similar organic matter, by fuming down with concentrated H_2SO_4 and HNO_3. When oxalic acid is heated with concentrated sulfuric acid it decomposes, yielding CO, CO_2 and other products. For the manipulative details of this step in the removal of interfering oxalates see the procedure on page 308.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of sodium oxalate test solution add a few drops of dilute NaOH and then $Ca(NO_3)_2$. What forms? Write the equation.

Filter off the precipitate, transfer it to a test tube and add 1 or 2 ml. of dilute $HC_2H_3O_2$. Does the solid appear to dissolve?

2. Decolorizing Test with $KMnO_4$. Treat the precipitated CaC_2O_4 obtained in experiment 1 with dilute H_2SO_4 and then add a drop or two of dilute $KMnO_4$. Observe the result. Write the equation showing the reduction of the MnO_4^- ion.

FLUORIDE, F^-

Most of the fluorides are insoluble in water, the notable exceptions being those of silver, mercury (ic), tin (ic), aluminum, sodium, potassium and ammonium.

Calcium fluoride is an important salt. It is formed when Ca^{++} is added to a soluble fluoride. CaF_2, like CaC_2O_4, is insoluble in

dilute acids, such as $HC_2H_3O_2$. The insolubility of CaF_2 in acetic acid serves to separate F^- as well as $C_2O_4^{=}$ from the other members of this group.

Fluorides are derived from the acid, hydrofluoric acid, which is a liquid boiling at 19.4° C. The commercial acid, dispensed in non-glass containers, is an aqueous solution containing about 50 per cent HF. It is a weakly ionized monobasic acid.

Hydrofluoric acid is formed when a fluoride, such as CaF_2, is treated with H_2SO_4; the equation is:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$

The most useful property of this acid is its ability to react with silica and silicates. Upon this property rests the test for fluorides, the etching test. With SiO_2 the acid forms silicon tetrafluoride:

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

In the case of glass, which is a silicate, the action of the acid leaves the surface etched.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of fluoride test solution, add some $Ca(NO_3)_2$ reagent. Record the equation for the reaction.

Without attempting to filter, add dilute acetic acid to the precipitated CaF_2. Does the precipitate dissolve? What other calcium salt of this group shows a similar behavior?

2. Etching Test. Precipitate CaF_2 from 5 ml. of fluoride test solution, filter and transfer the precipitate to a glass slide or plate of glass. Make a depression in the center of the mass. Coat the underside of a watch glass with paraffin wax and scratch some characters, such as your initials, through the waxed surface. Then add 2 or 3 drops of concentrated H_2SO_4 to the CaF_2, cover this with the watch glass and allow to stand for half an hour. Remove the wax from the watch glass and note what happened. Write the equations.

BORATE, BO_2^-, $B_4O_7^{=}$, $BO_3^{\equiv}$

The element boron forms three acids, namely orthoboric acid, H_3BO_3, metaboric acid, HBO_2, and tetraboric or pyroboric acid, $H_2B_4O_7$. Orthoboric acid, sometimes also called boracic acid, is

a white solid. Although it contains three replaceable hydrogens and therefore is tribasic, its primary ionization is rather feeble, taking place in accordance with the equation:

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$$

Boric acid behaves thus as a weak monobasic acid.

The commonest salt of boron is borax, or sodium tetraborate, $Na_2B_4O_7$, derived from tetraboric acid. Borax hydrolyzes first into free boric acid and the metaborate ion, which in turn hydrolyzes still further as shown in the equations:

$$B_4O_7^{=} + 3HOH = 2H_3BO_3 + 2BO_2^-$$

$$BO_2^- + 2HOH = H_3BO_3 + OH^-$$

A solution of borax therefore contains, in addition to $B_4O_7^{=}$ ions, free boric acid, metaborate ion and hydroxyl ions, and shows an alkaline reaction.

Calcium nitrate when added to a borax solution will precipitate the metaborate:

$$Ca^{++} + 2BO_2^- = \underline{Ca(BO_2)_2}$$

Barium nitrate produces a similar effect. Silver nitrate precipitates $AgBO_2$ from rather concentrated borax solutions; from dilute solutions containing a greater proportion of OH^-, Ag_2O is precipitated.

Some of the compounds of boron are volatile and burn with a green flame. Methyl borate, $(CH_3)_3BO_3$, and ethyl borate, $(C_2H_5)_3BO_3$, are two such compounds. These compounds are readily produced by the action of the corresponding alcohols on a solution of boric acid. In the case of methyl alcohol, the equation is:

$$H_3BO_3 + 3CH_3OH = (CH_3)_3BO_3 + 3H_2O$$

Borax, it will be recalled, is used in fused form as a bead test for cobalt and nickel. Refer to these bead tests under cobalt and nickel.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of borax test solution add $Ca(NO_3)_2$ reagent. What forms? Write the equation.

Add a little dilute acetic acid to the precipitate. Does it dissolve?

2. Turmeric Paper Test. Dip a strip of turmeric paper into a strong solution of borax, slightly acidified with HCl. After drying, the paper will turn reddish brown. The drying is best accomplished by placing the test paper on a watch glass and placing this in turn over a beaker of boiling water. The color will turn greenish black if the paper is afterwards moistened with a drop of NaOH.

3. Flame Test. Add a few milliliters of concentrated H_2SO_4 to 2 ml. of the borax test solution in a small evaporating dish and then add a little methyl alcohol. Stir the mixture and light the vapor. Observe the color of the flame. To what is the color due? The concentrated H_2SO_4 serves to remove the water formed in the reaction.

SULFITE, $SO_3^{=}$

The element sulfur forms a large number of acids. The more common ones for which detection is here provided are hydrosulfuric (hydrogen sulfide), H_2S, sulfurous, H_2SO_3, sulfuric, H_2SO_4, and thiosulfuric, $H_2S_2O_3$. The anion of sulfurous acid, the sulfite ion, is tested for in this group; sulfates are tested for in Group II, sulfides in Group III and thiosulfates in Group IV.

The free acid, sulfurous acid, H_2SO_3, is unstable and exists only in solution. It is formed by dissolving the anhydride, SO_2, a gas, in water:

$$SO_2 + H_2O = H_2SO_3$$

In such an aqueous solution, most of the SO_2 remains as dissolved gas and very little is combined as H_2SO_3.

The acid ionizes, like all dibasic acids, in two stages:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

and

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{=}$$

giving rise to the bisulfite ion and the sulfite ion. The ionization constant for the primary stage is 1.7×10^{-2}; for the secondary stage the constant is 5×10^{-6}. Partial and complete neutralization of sulfurous acid by bases produces bisulfites and sulfites, respectively.

All sulfites, except those of the alkali metals, are practically insoluble in water. Most of the bisulfites, on the other hand, are soluble in water.

The most interesting and analytically useful property of sulfites, when acidified, and of sulfurous acid itself is a strong reducing action. Oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$ and I_2 are reduced, the $SO_3^=$ being oxidized to $SO_4^=$. The sulfite ion will likewise reduce $HgCl_2$ to Hg_2Cl_2 to form a distinctive white precipitate. The reaction is used as a test for $SO_3^=$, the reaction being:

$$SO_3^= + 2HgCl_2 + H_2O = \underline{Hg_2Cl_2} + SO_4^= + 2H^+ + 2Cl^-$$

But under certain conditions this anion may also act as an oxidizing agent. For example, toward H_2S it acts as an oxidant, in an acid solution:

$$H_2SO_3 + 2H_2S = 3S + 3H_2O$$

Calcium nitrate readily precipitates white $CaSO_3$. The precipitate is easily soluble in acids, even dilute $HC_2H_3O_2$. Acids stronger than acetic decompose sulfites with evolution of SO_2:

$$\underline{CaSO_3} + 2H^+ = H_2SO_3 + Ca^{++}$$

$$H_2SO_3 \rightarrow SO_2 + H_2O$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 2 ml. of the sodium sulfite test solution add some $Ca(NO_3)_2$ reagent. Note the formation of a precipitate. What is it? Write the equation.

Barium nitrate and zinc nitrate produce similar precipitates. With $AgNO_3$, white Ag_2SO_3 is produced; this decomposes on boiling.

Treat the $CaSO_3$ obtained above with dilute $HC_2H_3O_2$. Note what takes place and write the equations.

2. Nitroprusside Test for Sulfites. To 1 ml. of saturated $ZnSO_4$ solution in a test tube add several drops of sodium nitroprusside solution. To this add 1 ml. of sulfite test solution. A dark red solution should result. Add several drops of potassium ferrocyanide solution and note that a white precipitate forms upon which the red color is adsorbed.

3. Reducing Action of the Sulfite Ion. To 8 or 10 ml. of hot, saturated mercuric chloride solution add a few milliliters of Na_2SO_3 test solution. What is the white precipitate? Record the reaction in your notebook.

ARSENITE, AsO_2^-

Arsenites, in their relation to the detection of arsenic among the cations, have already been partly discussed in division B of Group II of the cations, to which the student should now refer (see page 151). The most important of the trivalent forms of arsenic are meta-arsenious acid, $HAsO_2$, and the sulfide, As_2S_3. The acid is derived from As_2O_3, which when dissolved in water first forms the ortho-acid, which then passes over into the meta form:

$$As_2O_3 + 3H_2O = H_3AsO_3$$

$$H_3AsO_3 \rightleftharpoons HAsO_2 + H_2O$$

The oxide is soluble in acids and in bases; this shows it to be amphoteric. The acid exists only in solution. The test solution, $NaAsO_2$, is derived from the meta acid.

Many arsenites are insoluble in water. Thus, calcium meta-arsenite is readily precipitated by calcium ion as $Ca(AsO_2)_2$:

$$Ca^{++} + 2AsO_2^- = \underline{Ca(AsO_2)_2}$$

This precipitate dissolves in acetic acid as well as stronger acids.

The arsenite ion is a strong reducing agent and is easily oxidized by oxidizing agents, especially in acid solution. Thus if a mixture of arsenite and chromate, such as one might have in an "unknown," is acidified, rapid reduction of the dichromate to chromic ion takes place.

$$Cr_2O_7^{=} + 2H^+ + 3AsO_2^- = 2Cr^{+++} + H_2O + 3AsO_4^{\equiv}$$

This reduction takes place to a slight extent even in an alkaline solution, but not sufficiently to make the detection of arsenite impossible.

Potassium permanganate is reduced and decolorized by the arsenite ion in an acid solution and for this reason, when $KMnO_4$ is used as the test reagent for oxalates, arsenites as well as sulfites must be thoroughly washed out of the CaC_2O_4 residue.

The oxidizing agent used to detect arsenites is iodine; the reaction is:

$$AsO_2^- + I_2 + 2H_2O \rightleftharpoons AsO_4^{\equiv} + 2I^- + 4H^+$$

Special attention is called to this reversible reaction since the test for arsenates, as described later, consists of reducing the arsen-

ate with the iodide ion. The reaction is the reverse of the above reaction.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of $NaAsO_2$ test solution add a little $Ca(NO_3)_2$ reagent. Write the equation.

Treat the precipitate with dilute $HC_2H_3O_2$ and note what happens.

2. Test for Arsenite. To several milliliters of arsenite test solution add a few drops of starch solution, as indicator, and then a few drops of dilute (0.01 *N*) iodine solution. Is the starch-iodine complex decolorized? Write the equation showing the reduction of the iodine.

ARSENATE, $AsO_4^{\equiv}$

Arsenates are derived from arsenic acid; this, in turn, may be formed in aqueous solution by dissolving the anhydride, As_2O_5, in water:

$$As_2O_5 + 3H_2O = 2H_3AsO_4$$

Arsenic acid as a tribasic acid undergoes ionization in three stages, producing the primary, secondary and tertiary arsenate ions, $H_2AsO_4^-$, $HAsO_4^=$ and $AsO_4^{\equiv}$, respectively. Arsenates are analogous to the corresponding orthophosphates. The anion test solution is made from disodium arsenate, Na_2HAsO_4.

Calcium nitrate precipitates the normal or tertiary arsenate:

$$3Ca^{++} + 2AsO_4^{\equiv} = \underline{Ca_3(AsO_4)_2}$$

readily soluble in dilute $HC_2H_3O_2$.

The tests for arsenic, as described on page 166 and carried out in the scheme for the detection of cations, consist in the precipitation of (1) ammonium arsenomolybdate, $(NH_4)_3AsO_4 \cdot 12MoO_3$; (2) magnesium ammonium arsenate, $MgNH_4AsO_4$, and (3) Ag_3AsO_4. In the presence of phosphates these tests for $AsO_4^{\equiv}$ cannot be performed, since the $PO_4^{\equiv}$ ion produces similar results with the reagents employed.

The test recommended here consists of the reduction of the arsenate ion with potassium iodide in a strongly acid solution:

$$AsO_4^{\equiv} + 2I^- + 4H^+ \rightleftharpoons AsO_2^- + I_2 + 2H_2O$$

This is the reverse of the test for the arsenite ion in which the latter is oxidized by iodine.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Add to 2 ml. of arsenate test solution a few drops of dilute NaOH and then $Ca(NO_3)_2$ reagent until precipitation is complete. Write the equation.

Treat the precipitate with acetic acid. Does it dissolve?

2. Test for Arsenate. Add 1 ml. of concentrated HCl to 2 ml. of arsenate test solution and then add potassium iodide. To what is the brown color due? Write the equation. Compare this test with the test for arsenites.

PHOSPHATE, $PO_4^{\equiv}$

The element phosphorus forms three well-known phosphoric acids, namely orthophosphoric acid, H_3PO_4, metaphosphoric acid, HPO_3, and pyrophosphoric acid, $H_4P_2O_7$. It also forms phosphorous acid, H_3PO_3. Only the orthophosphoric acid will be considered here.

Orthophosphoric acid, in the pure state, is a white solid. Ordinarily, it is a thick syrupy solution containing about 85 per cent of H_3PO_4. It ionizes in three stages:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=$$

$$HPO_4^= \rightleftharpoons H^+ + PO_4^{\equiv}$$

the extent of the ionization of a 0.1 M solution being, respectively, 27, 0.1 and 0.0001 per cent.

Orthophosphoric acid forms three series of salts, derived by the successive neutralization of the three replaceable hydrogens and known as primary, secondary and tertiary orthophosphates.

Phosphates when in solution undergo partial hydrolysis according to the equations:

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^= + OH^-$$

$$HPO_4^= + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$$

The test solution used in the laboratory is prepared from the

disodium salt, Na_2HPO_4. Most of the phosphates are insoluble in water; practically all are soluble in acids. From a practically neutral solution of Na_2HPO_4, calcium nitrate will precipitate $CaHPO_4$:

$$Ca^{++} + HPO_4^{=} = \underline{CaHPO_4}$$

In a strongly alkaline solution, such as exists during the group precipitation, the addition of $Ca(NO_3)_2$ produces mainly the normal phosphate, $Ca_3(PO_4)_2$. This compound is soluble in dilute acetic acid. Barium, zinc and silver ions form similar insoluble phosphates.

Like the arsenate ion, $PO_4^{\equiv}$ will react with ammonium molybdate in a nitric acid solution to form a finely crystalline yellow precipitate of ammonium phosphomolybdate. The ionic equation is:

$$PO_4^{\equiv} + 12MoO_4^{=} + 24H^+ + 3NH_4^+ =$$
$$\underline{(NH_4)_3PO_4 \cdot 12MoO_3} + 12H_2O$$

In molecular form this equation becomes:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 =$$
$$\underline{(NH_4)_3PO_4 \cdot 12MoO_3} + 12H_2O + 21NH_4NO_3$$

In the systematic detection of phosphates in samples which also contain arsenates, this reaction can only be utilized as a test for phosphates, after the removal of the arsenic. In the scheme outlined later, arsenates, as well as arsenites, are precipitated and removed by treatment with H_2S.

With magnesia mixture, the $PO_4^{\equiv}$ ion, like the $AsO_4^{\equiv}$ ion, forms a white crystalline precipitate of magnesium ammonium phosphate:

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} = \underline{MgNH_4PO_4}$$

This reaction, it will be recalled (see Magnesium, page 211), is an important one for the separation, detection and determination of magnesium.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Place 2 ml. of $NaHPO_4$ test solution in a test tube, make alkaline with NaOH and then add $Ca(NO_3)_2$ reagent. Write the equation.

Treat the precipitate with dilute $HC_2H_3O_2$. Does it dissolve?

2. Test for Phosphates. To 5 ml. of test solution, add 5 ml. of concentrated HNO_3, 5 ml. of NH_4NO_3 reagent and then 10 ml. of ammonium molybdate reagent. Warm the solution. Allow to stand for some time in case precipitation does not take place at once. Write the equation for the reaction.

TARTRATE, $C_4H_4O_6^{=}$

Tartaric acid and alkali tartrates are important analytical reagents. Among the better known salts are "Rochelle salt," $NaKC_4H_4O_6$, cream of tartar, $KHC_4H_4O_6$, and tartar emetic, $(SbO)KC_4H_4O_6$. Tartaric acid is a white crystalline solid, soluble in water. As a weak dibasic acid it ionizes in two stages:

$$H_2C_4H_4O_6 \rightleftharpoons H^+ + HC_4H_4O_6^-$$

and

$$HC_4H_4O_6^- \rightleftharpoons H^+ + C_4H_4O_6^{=}$$

yielding the acid tartrate ion and the normal tartrate ion, respectively.

The most important property of the alkali tartrates is the readiness with which they form soluble complex ions with many metallic ions, such as Al^{+++}, Cr^{+++}, Fe^{+++}, Co^{++}, Ni^{++}, Cu^{++}, Sb^{+++}, Sn^{++++}, etc. For this reason, in the presence of a tartrate, many of the metallic ions fail to precipitate as hydroxides when treated with alkalies. It is important therefore to test for tartrates and effect their removal in the systematic procedures for cation detection. Citrates, malates, sugars, starches and many other forms of organic materials behave similarly.

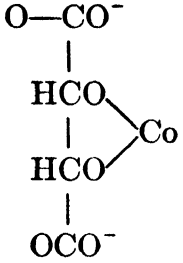
Tartaric acid has the structural formula shown below and when ionized yields the tartrate ion, which may have either of the two formulas:

$$\begin{array}{ccccc}
\mathrm{OCOH} & & \mathrm{OCO^-} & & \mathrm{OCOH} \\
| & & | & & | \\
\mathrm{HCOH} & \rightleftharpoons 2H^+ + & \mathrm{HCOH} & \text{or} & \mathrm{HCO^-} \\
| & & | & & | \\
\mathrm{HCOH} & & \mathrm{HCOH} & & \mathrm{HCO^-} \\
| & & | & & | \\
\mathrm{OCOH} & & \mathrm{OCO^-} & & \mathrm{OCOH}
\end{array}$$

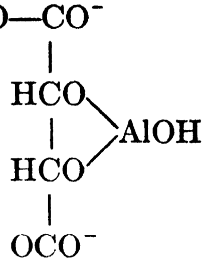
(tartaric acid)

In the cases of cobalt and aluminum, the structures of the com-

plexes are probably:



and



PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of test solution (50 milligrams) add a few drops of dilute NaOH and then $Ca(NO_3)_2$ slowly until an excess has been added. This results in the intermediate formation of a complex calcium tartrate ion, and the excess precipitates the calcium tartrate.

Add sufficient dilute acetic acid to the precipitate to dissolve it. Note particularly that, in this respect, tartrates differ from oxalates and fluorides.

The following experiments will reveal some of the distinctive properties of tartrates.

2. Charring Test for Tartrates. Heat a small amount of solid tartaric acid or sodium tartrate in a small evaporating dish. Notice how the mass darkens and chars and gives off an odor like that of burnt sugar. The heating decomposes the tartaric acid, with the formation of CO, CO_2, H_2O and carbon and other products having odors. Repeat the experiment but add a few drops of concentrated H_2SO_4 before heating. A similar effect takes place accompanied by the further oxidation of the carbon.

Tartrates, which interfere with the precipitation of cations, are tested for and removed by this means, during the systematic detection of the cations of Group III.

3. Silver Mirror Test. In a clean test tube, place 2 or 3 ml. of $AgNO_3$ solution and add, dropwise, dilute NH_4OH until a precipitate of Ag_2O appears and again dissolves. Then add 1 ml. of tartrate test solution and heat slowly. The tartrate reduces the Ag_2O to metallic silver which deposits on the walls as a bright mirror.

4. Resorcinol Test for Tartrate. To 3 ml. of concentrated sulfuric acid add carefully 2 drops of an aqueous, 2 per cent resorcinol solution. The solution will turn a light amber color. Then add several drops of the tartrate test solution and heat gradually. A dark red-violet solution should result.

REVIEW EXERCISES — SET 16

1. Write ionic equations showing the formation of the calcium salts of this group. What ions of this group are reducing in their nature? Name the oxidizing ion of this group. What means is taken to prevent the interaction of oxidizing and reducing ions in this systematic scheme?

2. Why is CO_2 liberated when $CaCO_3$ is treated with dilute $HC_2H_3O_2$? Give the equilibria involved. Why does $HC_2H_3O_2$ fail to dissolve CaC_2O_4?

3. Complete and balance, using half-cell reactions, the equations representing the action of:

(*a*) $KMnO_4$ on $H_2C_2O_4$ in H_2SO_4 solution $\rightarrow$
(*b*) $HgCl_2$ on $H_2SO_3 \rightarrow$
(*c*) I_2 on $AsO_2^- \rightarrow$
(*d*) I^- on $AsO_4^{\equiv} \rightarrow$

4. Write the equation for the phosphate test, using ammonium molybdate in a nitric acid solution. Show, by writing the corresponding equation for H_3AsO_4, why arsenates must be removed before the molybdate test is decisive for phosphates.

5. What relation do the tests for arsenite and arsenate have with respect to the presence of arsenic in a sample of material as referred to a cation analysis?

6. In a systematic analysis of a sample of material a white precipitate was found to form when $Ca(NO_3)_2$ was added to a basic solution of the anions. No anion of Group I could be detected. Account for this result.

7. Combine the equation for the arsenite test with that for the arsenate test into a reversible reaction. Explain how it is possible to use this reversible reaction as tests for both anions.

8. Calculate the gram-ion quantity of Ca^{++} ion required to start the precipitation of CaC_2O_4 in 5 ml. of test solution containing 50 milligrams of $C_2O_4^{=}$ ion. $K_{s.p.}$ of CaC_2O_4 is 2.6×10^{-9}.

9. What volume of 1 *M* $Ca(NO_3)_2$ must be used to precipitate completely the $CO_3^{=}$ contained to 5 ml. of test solution (1 ml. = 10 milligrams)?

10. Complete and balance the equations for the oxidation of:

(*a*) $SO_3^{=}$ by MnO_4^- in an acid solution;
(*b*) $SO_3^{=}$ by $Cr_2O_7^{=}$ in an acid solution;
(*c*) AsO_2^- by MnO_4^- in an acid solution;
(*d*) AsO_2^- by $Cr_2O_7^{=}$ in an acid solution.

Outline of Method of Analysis of This Group

The group is precipitated as a whole by $Ca(NO_3)_2$. The calcium salts are all white, hence no distinguishing color can be used to indicate the presence of any one anion. Moreover, in the strongly basic solution, some calcium hydroxide may precipitate; this renders the group reagent useless as a preliminary test for the presence of members of this group.

The solution is kept alkaline with NaOH in order to lessen, as far as possible, the interaction of oxidizing and reducing ions.

By the use of dilute acetic acid, (*a*) the calcium carbonate is decomposed with liberation of CO_2, (*b*) CaC_2O_4 and CaF_2 remain insoluble and (*c*) all other calcium salts are dissolved.

In the solution resulting from the action of acetic acid, tests can be made directly for borate, sulfite, arsenite and arsenate, by methods already described under preliminary experiments.

In order to identify the phosphate ion, the arsenate ion must be removed. This is accomplished by first reducing the latter to the arsenite form and then precipitating and separating it as As_2S_3.

Mention should be made of the possible presence of silicates. If silicate is present in soluble form, a part of it at least will be precipitated as calcium silicate and remain in the residue insoluble in acetic acid. A special method is described on page 319 for the detection of silicates.

Practice Analysis of a Mixture Consisting of Carbonate, Oxalate, Fluoride, Metaborate, Sulfite, Arsenite, Arsenate, Phosphate and Tartrate Ions

Place in a beaker 5 ml. of each of the test solutions of the anions of this group. Add 2 ml. of 4 *M* NaOH and then, with constant stirring, add 10 ml. of 1 *M* $Ca(NO_3)_2$ reagent. Heat the solution to boiling, allow to settle and filter off the precipitate, washing it twice with 10-ml. portions of water. There will be precipitated the calcium salts of these ions along with some calcium hydroxide. The reactions are represented by the following equations:

$$CO_3^{=} + Ca^{++} = \underline{CaCO_3}$$

$$C_2O_4^{=} + Ca^{++} = \underline{CaC_2O_4}$$

$$2F^- + Ca^{++} = \underline{CaF_2}$$

$$2BO_2^- + Ca^{++} = \underline{Ca(BO_2)_2}$$

$$SO_3^{=} + Ca^{++} = \underline{CaSO_3}$$

$$2AsO_2^- + Ca^{++} = \underline{Ca(AsO_2)_2}$$

$$2AsO_4^{\equiv} + 3Ca^{++} = \underline{Ca_3(AsO_4)_2}$$

$$2PO_4^{\equiv} + 3Ca^{++} = \underline{Ca_3(PO_4)_2}$$

$$C_4H_4O_6^{=} + Ca^{++} = \underline{CaC_4H_4O_6}$$

$$2OH^- + Ca^{++} = \underline{Ca(OH)_2}$$

Separation of Carbonate, Oxalate and Fluoride. If these calcium salts are treated with dilute acetic acid, the calcium carbonate will be decomposed with evolution of CO_2; the CaC_2O_4 and CaF_2 remain undissolved while the other calcium salts dissolve. The effect of the acid is shown below:

$$\underline{CaCO_3} + 2H^+ \rightarrow H_2CO_3 + Ca^{++}$$

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

$$\underline{CaC_2O_4} + 2H^+ \rightarrow \text{no action}$$

$$\underline{CaF_2} + 2HC_2H_3O_2 \rightarrow \text{no action}$$

$$\underline{Ca(BO_2)_2} + 2H^+ \rightarrow 2HBO_2 + Ca^{++}$$

$$\underline{CaSO_3} + 2H^+ \rightarrow H_2SO_3 + Ca^{++}$$

$$\underline{Ca(AsO_2)_2} + H^+ \rightarrow HAsO_2 + Ca^{++}$$

$$\underline{Ca_3(AsO_4)_2} + 3H^+ \rightarrow H_3AsO_4 + Ca^{++}$$

$$\underline{Ca_3(PO_4)_2} + 3H^+ \rightarrow H_3PO_4 + Ca^{++}$$

$$\underline{CaC_4H_4O_6} + 2H^+ \rightarrow H_2C_4H_4O_6 + Ca^{++}$$

$$\underline{Ca(OH)_2} + 2H^+ \rightarrow 2H_2O + Ca^{++}$$

Identification of Carbonate. Have at hand a platinum wire, in the loop of which is held a drop of $Ba(OH)_2$ reagent. Treat the group precipitate with 25 ml. of dilute (12.5 per cent) acetic acid, at the same time holding the drop of barium hydroxide in the escaping gas. It will be observed that vigorous effervescence takes place during the evolution of CO_2 and the drop of alkaline reagent turns turbid. These observations constitute the test for carbonates.

Dilute the acetic acid solution with 25 ml. of water, filter off the precipitate and wash it repeatedly with small portions of water, until separate portions of the washing no longer show a reducing action. This complete washing is necessary to remove the last traces of sulfite or arsenite which may remain in the precipitate. The reducing test is carried out by adding a drop of very dilute iodine solution containing starch as an indicator, to a small volume of the washings; the blue color of the starch will no longer be dis-

charged after sulfide or arsenite have been thoroughly extracted from the residue.

Identification of Oxalate. Treat the residue of CaC_2O_4 and CaF_2 on the filter paper with 20 ml. of hot, dilute H_2SO_4 and wash once with 10 ml. of water. The filtrate from this contains the oxalate ion. Take 5 ml. of this solution, heat it to boiling and add a few drops of 0.002 *M* $KMnO_4$ solution. The decolorizing of the permanganate solution, owing to reduction to Mn^{++}, shows the presence of the oxalate ion.

Identification of Fluoride. The residue remaining after the removal of CaC_2O_4 is CaF_2. The etching test for fluorides is conducted as follows: Coat a small watch glass with paraffin and make a scratch or some characters through the paraffin coating, in the central portion of the watch glass. Transfer the CaF_2 to a glass plate or slide, heap it up into a little cone and make a deep depression in the center. Place a few drops of concentrated H_2SO_4 in the crater, cover with the watch glass and set aside. At the end of about a half-hour, examine the watch glass and note that the glass where the surface was exposed by the scratch is etched by the hydrofluoric acid evolved from the calcium fluoride.

Identification of Borate. Take 2 ml. of the filtrate from the acetic acid treatment of the group precipitate and evaporate almost to dryness. Add a drop of concentrated HCl. Moisten a piece of turmeric paper with this solution, place on a watch glass over a beaker of boiling water and allow the paper to dry. A pink coloration imparted to the paper shows the presence of borate. If no coloration results on the first drying, the test paper should be treated again as before. To make doubly sure, treat the spot with a drop of NaOH; the color should change to a dull green.

Identification of Sulfite. On a watch glass place a few drops of saturated $ZnSO_4$ solution, a drop or two of $K_4Fe(CN)_6$ solution, together with several drops of sodium nitroprusside reagent. Then add a drop of the filtrate from the acetic acid treatment. The red color produced identifies the sulfite ion in the test mixture.

To confirm this, take a small portion of the acetic acid filtrate and to it add 10 ml. of a hot, saturated solution of $HgCl_2$. The white crystalline precipitate which should form is Hg_2Cl_2.

Identification of Arsenite. To 5 ml. of the boiled filtrate, from which sulfite has been completely removed, add 5 ml. of water in order to reduce the acidity. Then add a few drops of starch solu-

tion and a few drops of dilute 0.005 *M* iodine solution. The iodine will be reduced by the arsenite, with the disappearance of the blue color.

Identification of Arsenate. To another 5-ml. portion of the boiled solution add 5 ml. of concentrated HCl and a small quantity of potassium iodide. The iodide ion becomes oxidized by the arsenate ion to free iodine which gives a brown coloration to the solution.

Identification of Phosphate. Take 20 ml. of the boiled solution, add about 1 gram of sodium sulfite in order to reduce the arsenate to arsenite, make strongly acid by adding 2.5 ml. of concentrated HCl, heat to boiling and pass in hydrogen sulfide until precipitation of As_2S_3 is complete.

Filter off and discard the arsenious sulfide. Boil the filtrate to expel the excess of H_2S. The complete removal of H_2S should be tested for by holding over the boiling solution a strip of lead acetate paper, which will become black in the presence of H_2S. Hydrogen sulfide must be fully eliminated because if present, even in traces, it will reduce the ammonium molybdate reagent used in the phosphate test.

The filtrate, now free from arsenic and hydrogen sulfide, can be tested for phosphates. Add to 5 ml. of this an equal volume of water, 5 ml. of concentrated HNO_3, 1 gram of NH_4NO_3 and finally 10 ml. of ammonium molybdate solution. Heat this mixture nearly to boiling. The yellow precipitate which forms is ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$. It may require several minutes of standing before the precipitate forms.

Identification of Tartrate. Transfer the remainder of the solution to a small evaporating dish, evaporate nearly to dryness and then add a few drops of concentrated H_2SO_4. Charring, accompanied by the odor of burnt sugar, shows the presence of tartrates.

THE BARIUM NITRATE GROUP — GROUP II

SULFATE, $SO_4^{=}$
CHROMATE, $CrO_4^{=}$

This group consists of the sulfate ion and the chromate ion. The precipitating agent is a 0.25 *M* solution of $Ba(NO_3)_2$ and this, when added to a mixture of anions from which the insoluble calcium salts have already been removed, will result in the pre-

cipitation of barium sulfate, $BaSO_4$, and barium chromate, $BaCrO_4$.

SULFATE, $SO_4^=$

Sulfates and bisulfates are derived from sulfuric acid. This acid is formed by the reaction of its anhydride, SO_3, with water:

$$SO_3 + H_2O = H_2SO_4$$

Concentrated sulfuric acid, as ordinarily dispensed in the laboratory, contains about 95 per cent H_2SO_4 in water and has a specific gravity of about 1.84. It ionizes almost completely, forming the bisulfate ion in the primary stage:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

The bisulfate (or acid sulfate) ion is weakly ionized:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^=$$

Most of the sulfates of the metals are soluble in water, the exceptions being $BaSO_4$, $SrSO_4$ and $PbSO_4$. $CaSO_4$, Ag_2SO_4 and Hg_2SO_4 are somewhat insoluble. The table on page 206 gives the solubilities of $BaSO_4$, $SrSO_4$ and $CaSO_4$ in water.

The most important compound is $BaSO_4$. It is precipitated as a white, finely crystalline solid, very insoluble in water, the solubility being 0.0023 gram per liter. It is practically insoluble in dilute acids.

The formation of $BaSO_4$ and its insolubility in dilute acids is the most characteristic property of the sulfate ion and constitutes its most important analytical reaction. The barium salts of all other anions, particularly $BaCrO_4$, are soluble in HCl and other strong acids.

If $BaSO_4$ is boiled with Na_2CO_3 a considerable part of the precipitate undergoes a metathetical reaction in which the constituent ions exchange partners. That is, $BaSO_4$ is transformed into $BaCO_3$ while the $SO_4^=$ and Na^+ ions are in solution as ionized Na_2SO_4. The reaction may be shown by the equation:

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + 2Na^+ + SO_4^=$$

Fusion with solid Na_2CO_3 is a more effective method of accomplishing the same effect. This is a general method of putting or rendering soluble many relatively insoluble substances and is applied specifically to the preparation of anion solutions for sys-

tematic analysis for the purpose of removing interfering cations. Attention has already been directed to this property in the discussion of carbonates and will again be referred to under the procedure for making the prepared anion solution, page 281.

PRELIMINARY EXPERIMENTS

1. Precipitation of $BaSO_4$. To 5 ml. of Na_2SO_4 test solution add dropwise the group reagent, $Ba(NO_3)_2$. Note the nature of the precipitate. Record the ionic equation for its formation.

2. Test for Sulfate. Add some dilute HCl to the test tube containing the precipitated $BaSO_4$. Does the precipitate dissolve? Why does this observation constitute a test for the sulfate ion?

CHROMATE, $CrO_4^{=}$ (or $Cr_2O_7^{=}$)

The existence of chromium in anion forms has already been pointed out under the study of chromium (page 186). Thus the amphoteric hydroxide, $Cr(OH)_3$, when treated with NaOH gives rise to the orthochromite, $CrO_3^{\equiv}$, and the metachromite, CrO_2^- ion. Chromic acid, H_2CrO_4, does not exist free in an aqueous solution, but on ionizing yields the $HCrO_4^-$ and the $CrO_4^{=}$ ion. Chromates such as K_2CrO_4 are derived from chromic acid. Dichromates are salts of dichromic acid, $H_2Cr_2O_7$. If a solution of a chromate, such as the K_2CrO_4 test solution, is acidified the color changes from yellow to reddish orange, showing the formation of the dichromate, $Cr_2O_7^{=}$ ion, the reaction being:

$$2CrO_4^{=} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O$$

Conversely, if a dichromate solution is made alkaline the chromate ion is produced and predominates in the solution:

$$Cr_2O_7^{=} + 2OH^- \rightleftharpoons 2CrO_4^{=} + H_2O$$

In both the chromate and the dichromate ion, the valence of the chromium is +6, and the predominance of one or the other forms depends solely on the hydrogen- and hydroxyl-ion concentrations.

The precipitation of $BaCrO_4$, even if doubt remains concerning the presence of chromate as judged by the yellow color of this ion, in itself constitutes a decisive test for chromates.

A further test is that with hydrogen peroxide; a blue color, sometimes transient, develops in an ether layer. This test has already been discussed under chromium, page 189.

It should be recalled that the formation of yellow $PbCrO_4$ constituted a good test for lead (see " Lead," page 125). Further, the precipitation of $BaCrO_4$ has been utilized not only in the separation of chromium but also in the separation of barium. $BaCrO_4$ unlike $BaSO_4$ is soluble in strong acids such as HCl and HNO_3.

The most favorable conditions under which $BaCrO_4$ is formed have already been referred to, first under chromium (see page 193) and the separation of this element as $BaCrO_4$ from zinc and, secondly, under barium (see page 207) and the separation of barium as $BaCrO_4$ from strontium and calcium. In the anion scheme, these conditions are adhered to and the solution being kept faintly acid in a buffered $HC_2H_3O_2$ solution.

The chromate ion is a strong oxidizing agent, especially when in acid medium where it is present as $Cr_2O_7^{=}$ and reacts energetically with a considerable number of reducing ions. This property must be carefully taken into account in the analysis of samples containing chromates or dichromates, not only in the anion scheme but also in the detection of cations.

Oxidizing action, in general, increases with increasing acidity and is minimized in alkaline solution, hence, in order to lessen the reaction with the consequent destruction of reducing ions, solutions for analysis containing chromates together with reducing ions are kept strongly basic with NaOH in the procedure of analysis.

PRELIMINARY EXPERIMENT

Precipitation of $BaCrO_4$. To 5 ml. of K_2CrO_4 test solution, add a few drops of dilute $HC_2H_3O_2$, about $\frac{1}{2}$ ml. of $NaC_2H_3O_2$, and then add $Ba(NO_3)_2$ reagent. Write the ionic equation showing the result.

REVIEW EXERCISES — SET 17

1. Show by chemical equations how H_2CrO_4 and $H_2Cr_2O_7$ ionize. Also show the relation between $CrO_4^{=}$ and $Cr_2O_7^{=}$ by suitable equations involving H^+ and OH^-.

2. The dichromate ion, in an acid medium, is a fairly strong oxidizing agent. To show this effect, complete and balance the following equations:

(a) $Cr_2O_7^{=} + H^+ + SO_3^{=} \rightarrow$
(b) $Cr_2O_7^{=} + H^+ + AsO_2^{-} \rightarrow$
(c) $Cr_2O_7^{=} + H^+ + S^{=} \rightarrow$
(d) $Cr_2O_7^{=} + H^+ + I^- \rightarrow$

3. Barium chromate is best precipitated in a faintly acid solution. If enough $HC_2H_3O_2$ and NH_4OH are added to make the resulting solution 0.1 *M*

with respect to $HC_2H_3O_2$ and 0.05 M with respect to $NH_4C_2H_3O_2$, what is the H^+ ion concentration? $K_{(ion)}$ of $HC_2H_3O_2 = 1.8 \times 10^{-5}$.

4. If a sample of material contains a chromate or dichromate and is subjected to the cation procedure, show by equations the chemical changes that are undergone. If a cation analysis of a sample shows the presence of chromium, what further information will an anion analysis yield regarding the form in which chromium may have been present?

5. Suppose that in a certain solution the concentration of $SO_4^=$ and $CrO_4^=$ are both 0.01, and Ba^{++} is gradually added. What is the ratio of $SO_4^=$ to $CrO_4^=$ when both $BaSO_4$ and $BaCrO_4$ are precipitating? See Table VI for $K_{s.p.}$ values.

Outline of Method of Analysis of This Group

The methods for the identification of the sulfate and chromate ions are so simple and are so fully described in the procedure which follows, that they need no mention here. It should, however, be remarked that the chromate ion, especially in an acid solution, is a very strong oxidizing ion and even under the conditions of this scheme partially oxidizes certain reducing ions. Experience with the scheme has shown that positive tests can nevertheless be obtained for reducing ions in the presence of the chromate or dichromate. It should be remembered that the chromate ion, during a cation analysis, is reduced and chromium is regularly detected in Group III of the cations.

Practice Analysis of a Mixture Containing Sulfate and Chromate Ions

Mix 5 ml. of Na_2SO_4 test solution with 5 ml. of K_2CrO_4 test solution. Transfer about half of the mixture to another test tube for the separate test for sulfate.

Identification of Sulfates. To this portion of the mixture, add dilute HCl until the solution is acid, then add the $Ba(NO_3)_2$ group reagent. In this acidified solution $BaCrO_4$ cannot form and the white precipitate which forms is $BaSO_4$.

Identification of Chromates. To the other half of the mixture add $Ba(NO_3)_2$ until precipitation is complete. The precipitate consists of $BaCrO_4$ and $BaSO_4$. Filter off the precipitate, discarding the filtrate. Treat the residue with dilute HCl, which will dissolve only the barium chromate. Catch the filtrate, now containing the $Cr_2O_7^=$ ion, in a test tube. Make this filtrate alkaline with dilute NH_4OH and then add enough dilute $HC_2H_3O_2$ to

render it *just* acid. This will result in the reprecipitation of yellow $BaCrO_4$ and constitutes a test for the chromate ion in the original mixture.

The oxidation test with hydrogen peroxide with the resultant blue color developed in an ether layer, as described under chromium in the cation tests, may, of course, be employed here as a confirmatory test.

THE ZINC NITRATE GROUP — GROUP III

SULFIDE, $S^{=}$
CYANIDE, CN^{-}
FERROCYANIDE, $Fe(CN)_6^{\equiv\equiv}$
FERRICYANIDE, $Fe(CN)_6^{\equiv}$

In a systematic analysis, these four anions, whose calcium and barium salts in general are soluble, are precipitated with zinc nitrate in the form of ZnS, $Zn(CN)_2$, $Zn_3K_2[Fe(CN)_6]_2$ and $Zn_2Fe(CN)_6$. The first three anions are reducing agents; the last is an oxidizing substance.

SULFIDE, $S^{=}$

Sulfides and bisulfides are the salts of hydrosulfuric acid, H_2S, better known as hydrogen sulfide. This gas, with which the student is already familiar, is slightly soluble in water, forming, at room temperatures a 0.1 M solution of the dibasic, weakly ionized acid. The ionization in water takes place according to the equations:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^=$$

for which equilibria the ionization constants are, $K_1 = 9 \times 10^{-8}$ and $K_2 = 1.2 \times 10^{-15}$.

The sulfides and bisulfides of the alkali metals and alkaline earths undergo hydrolysis while being formed by the neutralization of a weak acid by strong bases. For example, the test solution, Na_2S, reacts with water to form the bisulfide ion:

$$S^= + HOH = HS^- + OH^-$$

rendering the solution strongly alkaline. The HS^- ion undergoes further hydrolysis yielding H_2S:

$$HS^- + HOH = H_2S + OH^-$$

Attention has been called to the nonformation of sulfides of aluminum and chromium (see pages 186 and 188) because the insoluble hydroxides, $Al(OH)_3$ and $Cr(OH)_3$, form during the hydrolysis of the corresponding sulfides.

Regarding the precipitation of metal sulfides and their solubility relationships in various solvents, the group reactions of cation Groups II and III and the theory of sulfide precipitation should be reviewed at this time.

Hydrogen sulfide and acidified solutions of soluble sulfides are strong reducing agents, which are readily oxidized by oxidants, generally to free sulfur. Thus, $K_2Cr_2O_7$ is reduced to chromic salt, the ionic equation for the reaction being:

$$Cr_2O_7^{=} + 8H^+ + 3H_2S = 2Cr^{+++} + 7H_2O + \underline{3S}$$

$KMnO_4$ is reduced to manganous ion. Nitric acid is reduced to NO, with either the formation of sulfur or complete oxidation of the sulfide ion to $SO_4^{=}$. In the first case we have, as half-cell reactions:

$$NO_3^- + 4H^+ + 3e = NO + 2H_2O$$

$$S^{=} = S^{\circ} + 2e$$

or expressed in molecular form:

$$2HNO_3 + 3H_2S = 2NO + 4H_2O + \underline{3S}$$

The oxidation of the sulfide ion to the sulfate ion may be shown in ionic form by the equation:

$$S^{=} + 4H_2O = SO_4^{=} + 8H^+ + 8e$$

which, when combined with the equation for the reduction of the NO_3^- ion, gives:

$$8NO_3^- + 8H^+ + 3S^{=} = 8NO + 4H_2O + 3SO_4^{=}$$

or, expressed in molecular form:

$$8HNO_3 + 3H_2S = 8NO + 4H_2O + 3H_2SO_4$$

Toward sulfurous acid or acidified solutions of sulfites, H_2S acts as a reducing agent. The main product of the reaction is free sulfur; the sulfite ion is reduced to S and the sulfide ion is oxidized to S.

The reduction of iodine by H_2S is an important analytical reaction; it is used in the quantitative determination of sulfides and of H_2S:

$$I_2 + S^{=} = 2I^- + \underline{S}$$

Two tests for sulfides are recommended in the systematic procedure. One is based on the fact that a strip of moistened lead acetate paper becomes dark brown or black when exposed to H_2S:

$$H_2S + Pb(C_2H_3O_2)_2 = \underline{PbS} + 2HC_2H_3O_2$$

The other is a violet-red color produced by sodium nitroprusside, $Na_2Fe(CN)_5NO$, reagent when treated with an alkaline solution of a sulfide. This is a very sensitive test for the sulfide ion, but it is not given by gaseous H_2S.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of Na_2S test solution, add $Zn(NO_3)_2$ until precipitation is complete. Record the equation.

2. Lead Acetate Test. Saturate a strip of filter paper with lead acetate solution, or moisten a strip of lead acetate test paper. Add a few drops of dilute HCl to the precipitated ZnS obtained in experiment 1, meanwhile holding the test paper in the escaping gas. What happens? Write the reaction.

3. Sodium Nitroprusside Test. This reagent, $Na_2Fe(CN)_5NO$, reacts with alkaline sulfide solutions to give a violet-red color. Conduct the test as follows: To a few drops of the sulfide solution, rendered alkaline with NaOH, add a drop or two of a 1 per cent solution of the reagent.

CYANIDE, CN^-

Cyanides and the free acid, gaseous HCN, are violent poisons. It is recommended that cyanides be omitted from elementary courses. If, however, they are to be included they should be tested for at the beginning of the anion analysis of unknowns and due precautions taken against their dangerous character. *All experiments which involve the liberation of gases with materials suspected of containing cyanides should be carried out under the hood.*

The cyanide ion readily forms a number of complex ions as, for example, the complex silver, copper and cadmium ions previously

referred to in the discussion of the properties of these metals and the ferrocyanide and ferricyanide ions included in this group. The ease with which these complexes are formed often serves as a test for cyanides.

Acidification of a cyanide solution results in the liberation of gaseous HCN which has a characteristic odor of bitter almonds. The acid is a liquid at room temperature. Its aqueous solution is very weakly ionized; in fact it is weaker than carbonic acid. This accounts for the fact that solid soluble cyanides give off the odor of HCN. Soluble cyanides are extensively hydrolyzed:

$$CN^- + HOH = HCN + OH^-$$

rendering the solution strongly alkaline.

The cyanide ion can be converted to the ferrocyanide ion, by treatment, in an alkaline medium, with $FeSO_4$ solution. The ferrous hydroxide formed by the action of OH^- on Fe^{++}, further reacts to give ferrous cyanide, $Fe(CN)_2$. This dissolves in an excess of the cyanide solution to form the ferrocyanide ion:

$$Fe(CN)_2 + 4CN^- = Fe(CN)_6^{----}$$

This property is used as a test for cyanides, by further adding a solution of $FeCl_3$, which produces a heavy blue precipitate of ferric ferrocyanide (Prussian blue):

$$3Fe(CN)_6^{----} + 4Fe^{+++} = Fe_4[Fe(CN)_6]_3$$

The cyanide ion is oxidized to the thiocyanate ion by action of ammonium polysulfide:

$$CN^- + S^{=} = CNS^-$$

This property may be employed as a test for cyanides. As described below, after acidification, a drop or two of $FeCl_3$ will produce the deep red color of the ferric thiocyanate complex:

$$Fe^{+++} + 6CNS^- = Fe(CNS)_6^{\equiv}$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 2 ml. of KCN test solution add some $Zn(NO_3)_2$ reagent. Describe the result and give the equation.

2. Prussian Blue Test for Cyanides. To 5 ml. of cyanide test solution, made alkaline with NaOH, add a few milliliters of a freshly prepared solution of $FeSO_4$ and heat to boiling. Now acidify with dilute HCl and add a drop or two of $FeCl_3$ reagent. What forms? Give a set of equations showing the successive reactions involved.

3. Thiocyanate Test for Cyanides. Treat 2 ml. of cyanide test solution with ammonium polysulfide and evaporate the solution to dryness. Then add a few drops of dilute HCl to the residue until acid and finally add a drop of $FeCl_3$ solution. Note the result. Write equations for the two reactions involved.

FERROCYANIDE, $Fe(CN)_6^{\equiv}$

Ferrocyanic acid, $H_4Fe(CN)_6$, is a white solid, soluble in water, unstable and easily oxidized in the air. The potassium salt, $K_4Fe(CN)_6$, is an important analytical reagent. With the exception of the alkali and alkaline earth salts, all ferrocyanides are insoluble in water; however double salts of the alkali and alkaline earth elements, such as $CaK_2Fe(CN)_6$, are insoluble in water. Soluble ferrocyanides are yellow in color; a number of the insoluble ones are white, but most of them are colored.

Ferrocyanides are mild reducing agents and are oxidized to ferricyanides by oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$, Br_2 and H_2O_2. On heating or on treatment with concentrated H_2SO_4, they are decomposed into a variety of products such as CO, CO_2, HCN and NH_3.

The ferrocyanide ion reacts with many different cations to form insoluble products. With the Zn^{++} ion and $K_4Fe(CN)_6$ there is formed the salt, zinc potassium ferrocyanide, according to the equation:

$$3Zn^{++} + 2K^+ + 2Fe(CN)_6^{\equiv} = \underline{Zn_3K_2[Fe(CN)_6]_2}$$

Ferrous salt solutions, such as $FeSO_4$, react to give at first a light-colored precipitate of $K_2Fe[Fe(CN)_6]$ which quickly oxidizes in the air to Prussian blue, $Fe_4[Fe(CN)_6]_3$.

On the other hand, ferric salt solutions react directly to form Prussian blue:

$$4Fe^{+++} + 3Fe(CN)_6^{\equiv} = \underline{Fe_4[Fe(CN)_6]_3}$$

This reaction, it will be recalled, is used as a test for ferric iron. See, in this connection, the reactions of iron on page 182.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 2 ml. of freshly prepared potassium ferrocyanide, $K_4Fe(CN)_6$, test solution, add some $Zn(NO_3)_2$ reagent. Observe the result. Write the equation.

2. Reactions with Iron Solutions. To 2 ml. of $K_4Fe(CN)_6$ add a few drops of freshly prepared $FeSO_4$ solution. Observe any change that takes place in the color of the precipitate. Account for this.

To 2 ml. of ferrocyanide test solution add a few drops of $FeCl_3$. What forms? Write the equation.

FERRICYANIDE, $Fe(CN)_6^{\equiv}$

Ferricyanic acid, $H_3Fe(CN)_6$, is a brown solid, soluble in water. With bases it yields stable salts known as ferricyanides. With the exception of the alkali metal and alkaline earth salts, these salts are insoluble in water.

The ferricyanide ion is an oxidizing agent and is reduced to ferrocyanide by a number of reductants, even in alkaline solution. Thus the sulfide, arsenite, sulfite, iodide, etc., are apt to be destroyed in mixtures containing the ferrocyanide ion.

With $Zn(NO_3)_2$, the ferricyanide ion forms zinc ferricyanide:

$$3Zn^{++} + 2Fe(CN)_6^{\equiv} = \underline{Zn_3[Fe(CN)_6]_2}$$

Ferrous ions produce Turnbull's blue (ferrous ferricyanide), $Fe_3[Fe(CN)_6]_2$:

$$3Fe^{++} + 2Fe(CN)_6^{\equiv} = \underline{Fe_3[Fe(CN)_6]_2}$$

Ferric ions yield a brown soluble product, $Fe[Fe(CN)_6]$. For more detail concerning the reactions of iron with ferrocyanides and ferricyanides, see page 182.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 2 ml. of $K_3Fe(CN)_6$ test solution add $Zn(NO_3)_2$ reagent. What is formed? Write the equation.

2. Reactions with Iron Solutions. To 2 ml. of potassium ferricyanide test solution add a few drops of freshly prepared $FeSO_4$ solution. What is the common name for the precipitate which forms? Give the equation.

To 2 ml. of $K_3Fe(CN)_6$ test solution add a few drops of $FeCl_3$ solution. Note that the solution turns brown but no precipitate forms. What product is formed?

REVIEW EXERCISES — SET 18

1. What reagents, other than a lead salt solution, might one use to produce a black stain as a test for a sulfide? What would produce a yellow stain? An orange stain?

2. What volume of H_2S gas measured under standard conditions of temperature and pressure is evolved when the ZnS produced from 50 milligrams of Zn^{++} ion is treated with HCl.

3. Review the theory of sulfide precipitation as discussed previously under the cations and give the ionization reactions and equilibrium constants for H_2S.

4. Write the necessary equations showing the Prussian blue test for the cyanide ion.

5. Give formulas showing the composition of the complex ions which the CN^- ion forms with Ag^+, Cu^{++}, Cd^{++}, Fe^{++} and Fe^{+++}. Look up the instability constants for several of these complex ions.

6. What happens when the ferrocyanide ion is treated with Fe^{++}? With Fe^{+++}? When the ferricyanide ion is treated with Fe^{++}? With Fe^{+++}?

Outline of Method of Analysis of This Group

If all four of these anions are present in the same mixture considerable difficulty is experienced with their detection. The presence of the ferricyanide ion causes difficulty, not only in this group but in the detection of certain ions of other groups, on account of its strong oxidizing tendency and property to form colloidal solutions. It seems best, therefore, to exclude the ferricyanide from the practice mixture and, at the discretion of the instructor, to omit it from "general unknowns" as well. The identification of sulfide, cyanide and ferrocyanide can readily be made according to the procedure which follows. The tests are based on the experiments already studied.

Practice Analysis of a Mixture Containing Sulfide, Cyanide and Ferrocyanide Ions

Prepare a mixture consisting of 5 ml. of Na_2S, 5 ml. of NaCN and 5 ml. of $K_4Fe(CN)_6$ test solution. Add a few drops of dilute NaOH to make sure that the solution is sufficiently alkaline. Then add $Zn(NO_3)_2$ reagent until precipitation is complete. The precipitate will consist of ZnS, $Zn(CN)_2$ and $K_2Zn_3[Fe(CN)_6]_2$. Decant the supernatant liquid. Add a little water to the residue; shake to form a suspension.

Identification of Sulfide. Transfer a small amount of the suspended residue to a test tube, add dilute HCl and hold over the mouth of the tube a strip of moistened lead acetate test paper.

The evolved H_2S will form PbS on the paper, giving a dark- or black-colored spot.

Identification of Cyanide. Place another portion of the suspension in a small Erlenmeyer flask, add 5 ml. of water and then acidify with dilute HCl. Place over the mouth of the flask a piece of filter paper moistened with dilute NaOH. Heat the contents of the flask and boil for about a minute. Then treat the filter paper with 2 drops of freshly prepared $FeSO_4$ solution, acidify with one drop of concentrated HCl and finally one drop of $FeCl_3$ solution. The blue color which forms is Prussian blue, $Fe_4[Fe(CN)_6]_3$, precipitated by the ferrocyanide formed from the cyanide.

Identification of Ferrocyanide. To a third portion of the residue, made slightly acid with dilute HCl, add a few drops of $FeCl_3$ reagent. A blue precipitate will form. This is Prussian blue.

THE SILVER NITRATE GROUP — GROUP IV

THIOSULFATE, $S_2O_3^{=}$
THIOCYANATE, CNS^-
IODIDE, I^-
BROMIDE, Br^-
CHLORIDE, Cl^-

In the systematic scheme here employed for the separation of anions into groups, the anions of Groups I, II and III are removed successively by means of calcium, barium and zinc nitrate. Since most silver salts are relatively insoluble it is important that the ions of these preceding groups are completely precipitated and removed. Advantage is then taken of a solution of $AgNO_3$ to precipitate the ions of this group in the form of $Ag_2S_2O_3$, AgCNS, AgI, AgBr and AgCl. The $AgNO_3$ is a 5 per cent solution.

THIOSULFATE, $S_2O_3^{=}$

Thiosulfates are derived from the hypothetical acid, thiosulfuric acid, $H_2S_2O_3$. This acid cannot be isolated because, when a thiosulfate is treated with an acid, decomposition takes place; the final reaction products are sulfur, sulfur dioxide and water. The reactions during decomposition may be shown by the equations:

$$S_2O_3^{=} + 2H^+ = H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow H_2SO_3 + \underline{S}$$

$$H_2SO_3 \rightarrow \overline{SO_2} + H_2O$$

The best-known salt is sodium thiosulfate, $Na_2S_2O_3$, from which the test solution is prepared. The thiosulfate ion is a strong reducing agent; one of the most important analytical reactions is the reduction of iodine with $Na_2S_2O_3$:

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-$$

Certain other oxidizing agents, in acidified solutions, react toward the thiosulfate ion in exactly the same way as toward sulfites, since in both cases the sulfurous acid, produced upon acidification, acts as the reducing agent. $Na_2S_2O_3$ is the " hypo " of the photographer; it is used to dissolve the unreduced portions of the silver halide in the photographic film. With silver chloride, for example, it forms a complex ion:

$$\underline{2AgCl} + 3S_2O_3^{=} = Ag_2(S_2O_3)_3^{≡} + 2Cl^-$$

Many thiosulfates are insoluble in water; in concentrated solutions, calcium and barium thiosulfates are formed. Accordingly there is some possibility of precipitating the thiosulfate ion in Groups I and II.

PRELIMINARY EXPERIMENT

1. Action of Group Reagent. To 5 ml. of $Na_2S_2O_3$ slowly add $AgNO_3$ reagent. The precipitate obtained at first is $Ag_2S_2O_3$. This soon undergoes decomposition, as evidenced by the gradual change of color to yellow, orange, brown and black, owing to the formation of Ag_2S.

The presence of a thiosulfate in a sample of material, when the systematic scheme described in this book is followed, is recognized by the blackening of the group precipitate. In fact, this is the only test possible, owing to the decomposition of the silver thiosulfate into silver sulfide, which prohibits any other test with the group precipitate.

THIOCYANATE, CNS^-

Thiocyanates are salts of thiocyanic acid, HCNS, which is an unstable gas at ordinary temperatures. In aqueous solution HCNS is a strong acid. The salts are colorless excepting, of course, those containing a colored cation.

Thiocyanates resemble the halides in solubility, AgCNS, $Pb(CNS)_2$ and $Cu_2(CNS)_2$ being relatively insoluble and

$Hg(CNS)_2$ being only slightly soluble. These insoluble salts, however, readily dissolve in an excess of alkali thiocyanate to form complex ions of the type $Ag(CNS)_3^{=}$, $Hg(CNS)_4^{=}$, etc.

Silver nitrate precipitates curdy, white, silver thiocyanate, AgCNS, even in a solution strongly acid with dilute HNO_3. The precipitate is soluble in dilute ammonia.

A very sensitive reaction of the CNS^- ion is the formation of the blood-red complex ion with ferric ion:

$$Fe^{+++} + 6CNS^- = Fe(CNS)_6^{\equiv}$$

This reaction, it will be recalled, is likewise an extremely delicate test for iron. See, in this connection, page 183.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. Add $AgNO_3$ reagent to 5 ml. of KCNS test solution until precipitation is complete. Write the equation.

The precipitate is insoluble in dilute HNO_3 but soluble in NH_4OH. Decant the supernatant liquid, reserving the curdy, white precipitate for the test for this anion.

2. Test for Thiocyanate. To a few drops of KCNS test solution, add several drops of $FeCl_3$ reagent. Explain the color produced. Give the equation.

Take the AgCNS precipitate obtained in experiment 1; add a little water and then a few drops of $FeCl_3$. Note that the test is given, even in the saturated solution of AgCNS. This test can be made more effective by first boiling the precipitate with a strong solution of NaCl. The AgCNS is thus transposed into AgCl, leaving the CNS^- ion in solution.

IODIDE, I^-

The element, iodine, a dark crystalline solid and the heaviest member of the halogen family, forms a series of acids, of which hydriodic acid, or hydrogen iodide, HI, and iodic acid, HIO_3, are the most important. Iodides and iodates are derived from these two acids.

The iodide ion, I^-, is a strong reducing agent easily oxidized to free iodine, I_2, by a number of oxidizing agents. Free iodine and the iodate ion are good oxidizing agents.

Silver iodide is readily formed by the reaction:

$$Ag^+ + I^- = AgI$$

It is extremely insoluble in water and acid solvents. Ammonium hydroxide will not dissolve it. In this respect AgI differs from AgCl — a fact utilized in the separation of iodide from chloride. Ammonium polysulfide, however, transposes it into Ag_2S, the iodide ion being liberated; this property is employed in the systematic scheme of separation. The reaction probably takes place in accordance with the equation:

$$\underline{2AgI} + S^{=} = 2I^- + Ag_2S$$

The vigorous reducing action of the iodide ion enables it to be readily oxidized by a large number of oxidants. To show the analogy with bromides and chlorides, the effects of the following oxidizing agents have been listed (see comparative effects on bromide and chloride).

1. Chlorine Water. A saturated solution of chlorine in water rapidly oxidizes iodides to free iodine:

$$Cl_2 + 2I^- = I_2 + 2Cl^-$$

The iodine thus liberated can be dissolved in an organic solvent such as chloroform or carbon tetrachloride, where it appears as a purple layer. This reaction is sometimes employed as a test for iodides.

If an excess of chlorine water is used the iodine is further oxidized to the iodate form:

$$5Cl_2 + I_2 + 6H_2O = 2IO_3^- + 10Cl^- + 12H^+$$

2. Sodium Hypochlorite. This oxidant reacts like chlorine water:

$$OCl^- + 2I^- + 2H^+ = I_2 + H_2O + Cl^-$$

liberating iodine. This is the reagent employed for the detection of iodides in the scheme of analysis. The procedure for conducting the test is given below. This reagent will oxidize iodine to iodate in accordance with the equation:

$$I_2 + 5OCl^- + 2OH^- = 2IO_3^- + 5Cl^- + H_2O$$

3. Sulfuric Acid. Concentrated H_2SO_4 oxidizes solid iodides with the formation of I_2, H_2S and S. The first effect is the liber-

ation of HI which then reacts with the H_2SO_4 according to the equation:

$$H_2SO_4 + 8HI = H_2S + 4I_2 + 4H_2O$$

The iodine reacts further with H_2S to give free S.

4. Concentrated H_2SO_4 and MnO_2. The action of this mixture on iodides is like that on bromides and chlorides, liberating iodine:

$$2NaI + MnO_2 + 3H_2SO_4 = I_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

5. Potassium Permanganate. In a dilute sulfuric acid solution, iodides reduce $KMnO_4$:

$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{++} + 5I_2 + 8H_2O$$

6. Concentrated H_2SO_4 and $K_2Cr_2O_7$. If a mixture of a solid iodide and solid $K_2Cr_2O_7$ is heated with concentrated H_2SO_4, iodine is formed. The reaction is expressed by the equation:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6NaI = 3I_2 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4 + 3Na_2SO_4$$

Compare this with the corresponding reaction for bromides and chlorides. The same result is obtained when a dilute solution of the test substance is treated with dilute H_2SO_4 and $K_2Cr_2O_7$; the reaction is best expressed in ionic form:

$$Cr_2O_7^{=} + 14H^+ + 6I^- = 2Cr^{+++} + 7H_2O + 3I_2$$

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of KI test solution add the silver nitrate group reagent. Note the color of the precipitate. Divide the precipitate into several parts. Try the action of HNO_3 on one part. Treat another portion with dilute NH_4OH. To the third portion add ammonium polysulfide. Record your observations in each case.

2. Test for Iodides. Place 2 ml. of test solution in a test tube, add several milliliters of carbon tetrachloride and then add dropwise some sodium hypochlorite reagent; shake the test tube after the addition of each drop. Note what happens.

Continue addition of reagent until the color in the CCl_4 layer disappears. Explain what happens. Write the equations.

BROMIDE, Br^-

Bromine is a heavy, brown liquid. The important acids are hydrobromic acid (an aqueous solution of hydrogen bromide, HBr) and bromic acid, $HBrO_3$. The corresponding anions are the bromide, Br^-, and bromate, BrO_3^-.

Most of the bromides are water soluble, the exception being, like the iodides and chlorides, AgBr, $PbBr_2$, Hg_2Br_2 and Cu_2Br_2.

The group reagent, $AgNO_3$, precipitates pale yellow AgBr:

$$Br^- + Ag^+ = \underline{AgBr}$$

Silver bromide is insoluble in acid solvents. It will dissolve in ammonium polysulfide:

$$\underline{2AgBr} + S^= = 2Br^- + \underline{Ag_2S}$$

It is only partly soluble in NH_4OH.

The bromide ion is a fairly strong reducing agent, less energetic than iodides but more so than chlorides. Reactions showing the behavior of a number of oxidizing agents toward the bromide ion are here discussed. These properties should be compared with those of iodides and chlorides.

1. Chlorine Water. This reacts toward the bromide ion in the same manner as iodides, liberating bromine:

$$Cl_2 + 2Br^- = Br_2 + 2Cl^-$$

The liberated bromine can be extracted with chloroform or carbon tetrachloride, and gives to the organic solvent layer a reddish yellow color. This is a good test for bromides.

2. Sodium Hypochlorite. Bromides are oxidized to bromine by NaOCl

$$OCl^- + 2Br^- + 2H^+ = Br_2 + H_2O + Cl^-$$

in a solution made acid with dilute H_2SO_4. This method for the identification of bromides is utilized in the scheme of analysis and is outlined as a preliminary experiment.

3. Sulfuric Acid. Concentrated H_2SO_4 reacts with bromides, first to liberate HBr, which is at once oxidized to bromine:

$$H_2SO_4 + 2HBr = SO_2 + Br_2 + 2H_2O$$

4. Concentrated H_2SO_4 and MnO_2. A mixture of solid bromide, MnO_2 and concentrated H_2SO_4, when heated, evolves free

bromine. The reaction is analogous to that taking place with chlorides:

$$2NaBr + MnO_2 + 3H_2SO_4 = Br_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

5. Potassium Permanganate. Bromides will reduce an acidified solution of $KMnO_4$ with liberation of Br_2:

$$2MnO_4^- + 10Br^- + 16H^+ = 2Mn^{++} + 5Br_2 + 8H_2O$$

6. Concentrated H_2SO_4 and $K_2Cr_2O_7$. A mixture of NaBr and solid $K_2Cr_2O_7$, when treated and warmed with concentrated H_2SO_4, reacts to form bromine, according to the equation:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6NaBr = 3Br_2 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4 + 3Na_2SO_4$$

This reaction is similar to that of iodides but differs from that of chlorides.

In a dilute solution of $K_2Cr_2O_7$ acidified with dilute sulfuric acid, no reaction takes place; in this sense the behavior differs from that of iodides.

PRELIMINARY EXPERIMENTS

1. Action of Group Reagent. To 5 ml. of NaBr test solution, add $AgNO_3$ until precipitation is complete. Record the equation and color of the precipitate. Treat some of the AgBr with $(NH_4)_2S_2$. What change takes place?

2. Test for Bromides. In a test tube place 2 ml. of carbon tetrachloride and 2 ml. of NaBr test solution, made slightly acid with dilute H_2SO_4. Add sodium hypochlorite NaOCl solution, drop by drop. Observe the color developed in the organic liquid layer. Write the reaction.

CHLORIDE, Cl^-

Chlorine is the most widely distributed and abundant member of the halogen family. It is a gaseous element and forms a series of acids. Hydrochloric acid is the aqueous solution of hydrogen chloride and yields the chloride ion upon neutralization or dissociation. Other acids are hypochlorous, chlorous, chloric and perchloric, from which are derived hypochlorites, ClO^-, chlorites,

ClO_2^-, chlorates, ClO_3^- and perchlorates, ClO_4^-. Provision is made in this book for the detection of chlorides and chlorates. Some knowledge of the properties of sodium hypochlorite is also involved.

All chlorides are soluble in water with the exception of those of Group I of the cations, along with Cu_2Cl_2 and TiCl. Silver chloride is a curdy, white precipitate formed by the simple reaction:

$$Ag^+ + Cl^- = \underline{AgCl}$$

Silver chloride is insoluble in acids but dissolves in ammonia solution, forming with the latter reagent the diammono-silver ion. Silver bromide partially dissolves in ordinary ammonia solutions but silver iodide does not. AgCl is transposed by $(NH_4)_2S_2$.

The test for the chloride ion consists in acidifying, with dilute HNO_3, the ammonia complex obtained by dissolving AgCl in ammonia solution:

$$\underline{AgCl} + 2NH_3 = Ag(NH_3)_2^+ + Cl^-$$

Upon acidification with HNO_3, silver chloride is precipitated:

$$Ag(NH_3)_2^+ + Cl^- + 2H^+ = \underline{AgCl} + 2NH_4^+$$

This, it will be recalled, is the test for silver as well.

Since, however, silver bromide is partly soluble in ammonia and upon acidification would yield AgBr, hardly distinguishable from AgCl, this simple mode of procedure must be modified when analyzing mixtures which are shown or known to contain bromides. A specially prepared ammonia solution, known as ammoniacal silver nitrate or Miller's reagent, is used, in which the concentrations of NH_3 and $AgNO_3$ are so adjusted as to prevent the dissolving of the AgBr in the ammoniacal solvent. The reagent supplied is 0.25 *M* with respect to NH_4OH, 0.01 *M* with respect to $AgNO_3$ and contains in addition 0.25 of a gram-mole of KNO_3 per liter; the last ingredient aids in the coagulation of the AgCl. With the use of this reagent, it is found that enough AgCl dissolves to give the chloride test, but inappreciable quantities of AgBr or AgI dissolve to give misleading conclusions.

The effect of oxidizing agents on the chloride ion is here compared with that for bromides and iodides.

1. Chlorine Water. Obviously this reagent will have no effect on chlorides.

2. Sodium Hypochlorite. This reagent has no effect on the chloride ion.

3. Sulfuric Acid. Concentrated H_2SO_4 does not oxidize chloride but liberates free HCl when added to a solid chloride.

4. Concentrated H_2SO_4 and MnO_2. When a mixture of MnO_2 and a solid chloride is treated with concentrated H_2SO_4 and heated, chlorine is liberated. The equation for the reaction is:

$$MnO_2 + 2NaCl + 3H_2SO_4 = Cl_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

5. Potassium Permanganate. Chlorides are oxidized by $KMnO_4$ in an acidified solution according to the equation:

$$2MnO_4^- + 10Cl^- + 16H^+ = 2Mn^{++} + 5Cl_2 + 8H_2O$$

when the chloride-ion concentration is high and the solution is hot.

6. Concentrated H_2SO_4 and $K_2Cr_2O_7$. Solid $K_2Cr_2O_7$ and concentrated H_2SO_4 react with a solid chloride, such as NaCl, to form chromyl chloride, CrO_2Cl_2, a vapor which can be distilled and condensed. The reaction proceeds according to the equation:

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl = 2CrO_2Cl_2 + 3H_2O + 4NaHSO_4 + 2KHSO_4$$

This is the chromyl chloride test, sometimes employed for the detection of chlorides. The vapors are distilled into NaOH solution, in which the yellow color of the chromate ion which forms can be recognized. This latter reaction can be shown by the equation:

$$CrO_2Cl_2 + 4OH^- = 2Cl^- + CrO_4^{=} + 2H_2O$$

PRELIMINARY EXPERIMENT

1. Action of Group Reagent. Add some $AgNO_3$ reagent to 5 ml. of NaCl test solution. Filter off the precipitate and treat it with dilute ammonia solution. What happens? Acidify the resulting solution with dilute HNO_3. What is the precipitate which forms? Write the equations for the reactions which take place.

Repeat the experiment, using Miller's reagent instead of ordinary ammonia reagent. Record the result.

REVIEW EXERCISES — SET 19

1. Assemble the equations for the reactions taking place when the anions of this group are precipitated with $AgNO_3$. Write equations for the transposing of AgI, AgBr and AgCl by $(NH_4)_2S_2$.

2. How do AgCl, AgBr and AgI behave, respectively, toward NH_4OH? Explain the function of Miller's reagent in the separation of chlorides from bromides.

3. Calculate the volume of a 5 per cent solution of $AgNO_3$ required to precipitate 50 milligrams of Cl^- as AgCl. Do the same for the iodide.

4. Calculate the C_{Ag^+} required to start the precipitation of AgCl in 5 ml. of test solution containing 10 milligrams of Cl^- per milliliter. ($K_{s.p.}$ of AgCl = 1.1×10^{-10}.)

5. Show the method of balancing the following equations:

(*a*) For iodides: Property (2), (5), (6).
(*b*) For bromides: Property (2), (4), (5).
(*c*) For chlorides: Property (4), (6).

6. Calculate the C_{Ag^+} in a solution which is 0.1 *M* with respect to the complex salt $Ag(NH_3)_2Cl$, assuming complete ionization of the salt. The instability constant of $Ag(NH_3)_2^+$ is 7×10^{-8}.

7. Write and balance (by half-cell reactions) the reactions taking place when KI acts as a reducing agent, in H_2SO_4 solution, toward (*a*) $KMnO_4$; (*b*) $K_2Cr_2O_7$; (*c*) Na_3AsO_4.

8. Give a diagrammatic scheme for the detection of F^-, Cl^-, Br^- and I^- in an "unknown" solution.

9. Write out a scheme which will provide for the separation and detection of the following anions of sulfur: $SO_3^=$, $SO_4^=$, $S^=$, $S_2O_3^=$, CNS^-.

10. Give a procedure of analysis by which $PO_4^{\equiv}$, Cl^-, I^-, $AsO_4^{\equiv}$ and AsO_2^- can be detected in a sample of material.

Outline of Method of Analysis of This Group

Silver nitrate, as the group precipitant, will cause the formation of $Ag_2S_2O_3$, AgCNS, AgI, AgBr and AgCl. Owing to its unstable nature the silver thiosulfate rapidly undergoes decomposition, resulting finally in the formation of black silver sulfide, which in itself constitutes the test for the thiosulfate ion. Through the use of a ferric salt solution, the thiocyanate ion can readily be identified.

The silver salts of the group precipitate are then dissolved by ammonium polysulfide, in order to return the iodide, bromide and chloride to the ionic form. The identification of the iodide ion and the bromide ion is carried out by oxidizing these ions by means of NaOCl, the distinguishing colors appearing in a carbon tetrachloride layer.

To detect chloride in the presence of bromide and iodide, the ions are again reprecipitated as silver salts and then a specially pre-

pared ammonia solution, containing also $AgNO_3$ and KNO_3, known as Miller's reagent, is used to dissolve only the AgCl as ammono-silver complex. From this $Ag(NH_3)_2^+$ complex, silver chloride can then be reprecipitated.

PRACTICE ANALYSIS OF A MIXTURE CONTAINING THIOSULFATE, THIOCYANATE, IODIDE, BROMIDE AND CHLORIDE IONS

Make up a mixture consisting of 5 ml. of each of the five anions of this group. Render the solution *just* ammoniacal with dilute NH_4OH, testing carefully with litmus paper; add 1 ml. of NH_4OH in excess. Then add the group reagent, a 5 per cent solution of $AgNO_3$, until precipitation is complete. Heat the solution to boiling and then make it faintly acid with dilute HNO_3, adding the acid dropwise with constant stirring. After the precipitate has settled, filter and wash to remove the last traces of $AgNO_3$ remaining in the precipitate.

It will be observed that the precipitate rather quickly turns dark, owing to the decomposition of the $Ag_2S_2O_3$ into black Ag_2S. The following equations show the formation of the group precipitate:

$$S_2O_3^{=} + 2Ag^+ = \underline{Ag_2S_2O_3} \rightarrow \underline{Ag_2S}$$

$$CNS^- + Ag^+ = \underline{AgCNS}$$

$$I^- + Ag^+ = \underline{AgI}$$

$$Br^- + Ag^+ = \underline{AgBr}$$

$$Cl^- + Ag^+ = \underline{AgCl}$$

Identification of Thiosulfate. The darkening of the group precipitate during the addition of the $AgNO_3$ constitutes the test for thiosulfate.

Identification of Thiocyanate. Remove a small part of the group precipitate to a test tube, add 5 ml. of water and an equal volume of $FeCl_3$ solution. Shake the mixture and allow to settle. The solution will be colored deep red, owing to the formation of the ferric thiocyanate complex, $Fe(CNS)_6^{\equiv}$.

Identification of Iodide. The halide ions now remain to be identified. In order to test for these, the silver salts must be put back into solution. This is accomplished as follows. Transfer the remainder of the group precipitate to a beaker, add 15 ml. of am-

monium polysulfide and heat to boiling. This will dissolve the silver salts of these ions.

Acidify the solution with dilute H_2SO_4 in order to destroy the excess of polysulfide solvent. Heat to boiling to expel the hydrogen sulfide, filter off, wash twice and discard the residue, retaining the filtrate which now contains the halide ions.

To 5 ml. of this filtrate in a test tube add NH_4OH until, as shown by litmus, the solution is faintly alkaline. Now add 2 ml. of carbon tetrachloride and then *drop by drop* a solution of sodium hypochlorite. Shake the tube and note the violet color of the carbon tetrachloride layer. This is due to iodine liberated by the oxidation of the iodide ion by hypochlorite.

Identification of Bromide. To the same tube in which the iodide test was made, add more NaOCl until the violet color is discharged and all the iodine has been oxidized to the colorless iodate form. Then acidify with dilute H_2SO_4 and continue treatment with NaOCl, in order to oxidize the Br^- to Br_2. The brown color now formed in the CCl_4 layer shows the presence of bromine.

Identification of Chloride. To another 5 ml. portion of the solution containing the dissolved halides, add the $AgNO_3$ reagent until the precipitation of the silver salts is complete, heat to boiling and filter, discarding the filtrate. Wash the residue twice with 10 ml. of water.

Then treat the precipitate on the filter with 10 ml. of the Miller's reagent (specially prepared NH_4OH containing $AgNO_3$ and KNO_3). This reagent will attack the AgCl but not the AgBr nor AgI.

The filtrate from this ammoniacal silver nitrate now contains the chloride in the form of $Ag(NH_3)_2^+$. To 1 ml. of this filtrate add enough dilute HNO_3 to acidify the solution. AgCl will be reprecipitated.

THE SOLUBLE ANION GROUP—GROUP V

CHLORATE, ClO_3^-
ACETATE, $C_2H_3O_2^-$
NITRITE, NO_2^-
NITRATE, NO_3^-

Normally, this group includes the chlorate, acetate and nitrite ion, whose salts are relatively soluble and are not precipitated by any of the group reagents. The nitrate ion is here included for

discussion on account of its similarity with the nitrite ion; in a systematic analysis, nitrates must always be tested for in a portion of the original sample.

CHLORATE, ClO_3^-

Chlorates are salts of chloric acid. This acid exists only in moderately dilute solutions and is strongly ionized. $HClO_3$ and chlorates are vigorous oxidizing agents. *Warning:* The solid salts should never be ground or heated together with oxidizable substances nor heated with concentrated sulfuric acid, since reaction takes place with violent explosions.

All chlorates are soluble in water.

The chlorate ion may be reduced to chloride ion by reductants such as $NaNO_2$, in an acidified solution:

$$ClO_3^- + 3NO_2^- = Cl^- + 3NO_3^-$$

Other agents which will reduce chlorates are Na_2SO_3, H_2S and $FeSO_4$.

PRELIMINARY EXPERIMENT

Test for Chlorate. To 5 ml. of $KClO_3$ test solution add 2 ml. of dilute H_2SO_4 and then about 0.1 of a gram of solid sodium nitrite and heat to boiling. What change has taken place with the chlorate ion? Write the equation.

Then, after boiling, add 2 ml. of concentrated HNO_3 in order to destroy the excess of nitrite and finally add 2 ml. of $AgNO_3$ solution. What is the precipitate which forms?

The test can also be carried out with the use of an acidified solution of Na_2SO_3 instead of $NaNO_2$ for reducing the chlorate ion.

ACETATE, $C_2H_3O_2^-$

Acetates are salts of acetic acid. The student has already become familiar with this weakly ionized organic acid in connection with the calculation of ionization constants, common-ion effect and buffer solutions. The formula for the acid is written in organic chemistry as CH_3COOH; the formula, CH_3COO^-, or the symbol Ac are sometimes used rather than $C_2H_3O_2^-$ to denote the acetate ion.

If a solution containing the acetate ion is acidified with any strong acid, acetic acid will form:

$$H^+ + C_2H_3O_2^- = HC_2H_3O_2$$

This may be recognized by the vinegar-like odor.

The formation of esters (organic salts) of acetic acid is the basis of the test for acetates. Ethyl alcohol, C_2H_5OH, for example, reacts with acetic acid to form the organic ester, ethyl acetate, which possesses a sweet, fruity odor. The reaction is:

$$C_2H_5OH + HC_2H_3O_2 = C_2H_5C_2H_3O_2 + H_2O$$

Instead of ethyl alcohol, some chemists prefer to use amyl alcohol, $C_5H_{11}OH$, the ester formed being amyl acetate, $C_5H_{11}C_2H_3O_2$, which has the odor of bananas.

A delicate test for acetates depends upon the precipitation of basic lanthanum acetate and the adsorption of iodine by the precipitate. The test is conducted by adding to 5 ml. of acetate test solution 1 ml. of 5 per cent $La(NO_3)_3$ reagent, 1 ml. of (0.01 N) iodine solution and then adding dilute NH_4OH until a permanent precipitate remains. An intense blue color, similar to that produced by starch and iodine, forms. If the color is slow in forming, heat the solution to boiling and allow to stand for several minutes. This test invariably gives good results when applied to a pure acetate solution but sometimes fails when attempted in systematic analysis.

Some basic acetates are insoluble in water. Those of analytical importance are the basic acetates of ferric iron, aluminum and chromium. If, for example, $NaC_2H_3O_2$ is added to a ferric chloride solution, non-ionized $Fe(C_2H_3O_2)_3$ will form, coloring the solution red. If the solution is then diluted and boiled, hydrolysis takes place, precipitating basic ferric acetate according to the reaction:

$$Fe(C_2H_3O_2)_3 + 2HOH = \underline{Fe(C_2H_3O_2)(OH)_2} + 2HC_2H_3O_2$$

This behavior of iron toward acetates will again be referred to in Part IV.

PRELIMINARY EXPERIMENTS

1. Liberation of Acetic Acid. Add 2 ml. of dilute (1:1) sulfuric acid to a few milliliters of $NaC_2H_3O_2$ test solution, warm and note the odor. Explain why $HC_2H_3O_2$ is formed.

2. The Ester Test. Add a few milliliters of concentrated H_2SO_4 to a few milliliters of $NaC_2H_3O_2$ test solution, cool and then add 3 to 5 ml. of either ethyl alcohol or amyl alcohol. Warm the mixture and cautiously smell the vapors. Note and describe the odor. Do not confuse the odor of the alcohol used with that of the ester formed. Write the equation for the reaction.

NITRITE, NO_2^-

Nitrites are the salts of nitrous acid. HNO_2 is an unstable, weakly ionized acid, and is formed when a nitrite is treated with a stronger acid or by passing NO_2 into water:

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

All normal nitrites are soluble in water (silver nitrite, however, is only slightly soluble). Some complex nitrites, such as $K_3Co(NO_2)_6$ are quite insoluble (recall the test for potassium).

The most important and interesting property of nitrites is that they may act either as reducing or as oxidizing agents. Examples of both behaviors are given below.

Nitrites are easily decomposed by acids. When a nitrite is treated with dilute acid, such as HCl, the first action is the formation of nitrous acid:

$$NO_2^- + H^+ = HNO_2$$

This decomposes into nitric oxide, water and HNO_3:

$$3HNO_2 \rightarrow \overline{2NO} + H_2O + HNO_3$$

As the NO escapes into the air, it is oxidized to brown fumes of NO_2.

$$2NO + O_2 = \overline{2NO_2}$$

If a strip of starch-potassium iodide test paper is held in the escaping fumes, the iodide will be oxidized to I_2, coloring the paper blue.

A similar test may be made in the solution by adding a few drops of KI reagent and then acidifying with dilute acetic acid. The reaction that takes place is as follows:

$$2HI + 2HNO_2 = I_2 + \overline{2NO} + 2H_2O$$

The liberated iodine may be shown by adding a few drops of carbon tetrachloride, and then shaking. The iodine colors the carbon

tetrachloride layer an intense violet. Since certain other anions will liberate iodine from iodides, this reaction is not an infallible test for nitrites.

As already shown, when nitrites are treated with acids, nitrous acid as well as nitric acid forms as one of the products. Dilute acetic acid will bring about this decomposition of a nitrite but, in the case of a nitrate, concentrated sulfuric acid is required. This fact enables one to test for a nitrite in the presence of a nitrate by the so-called ferrous nitrosyl or " ring " test.

This test as applied to nitrites consists of treating the solution with dilute acetic acid and then adding a solution of ferrous sulfate. The Fe^{++} ion reduces the nitrous acid formed upon acidification:

$$NO_2^- + 2H^+ + Fe^{++} = NO + H_2O + Fe^{+++}$$

The NO then forms the complex ferrous nitrosyl ion which has a brown color:

$$Fe^{++} + NO = Fe(NO)^{++}$$

In the case of a nitrite the brown color appears throughout the solution, whereas in the case of a nitrate, when concentrated H_2SO_4 instead of $HC_2H_3O_2$ is used, the color appears as a ring at the junction of the two liquids which produces the brown coloration observed in the solution.

In applying this test to the detection of nitrites provision is made for the removal of anions which otherwise would interfere.

The nitrite ion is capable of oxidizing ammonium salts, the products being nitrogen and water:

$$NO_2^- + NH_4^+ = N_2 + 2H_2O$$

This reaction is used to destroy nitrites when the ring test is to be used for the detection of nitrates.

Urea is oxidized and nitrites reduced, with liberation of free nitrogen, when acidified solutions are allowed to react. The reaction takes place according to the equation:

$$CO(NH_2)_2 + 2NO_2^- + 2H^+ = CO_2 + 2N_2 + 3H_2O$$

The evolution of nitrogen observed during the reaction may serve as a test for nitrites. Moreover, the reaction may be employed to remove all but traces of nitrites in conducting the ring test for nitrates.

As a reducing agent, $NaNO_2$ is employed in reducing the chlorate ion to chloride ion:

$$ClO_3^- + 3NO_2^- = Cl^- + 3NO_3^-$$

This reaction proceeds only in acid solution, hence chlorates and nitrites are compatible as long as the mixture is not acidified. See Chlorates, page 265.

PRELIMINARY EXPERIMENTS

1. Decomposition of Nitrites by Dilute Acids. Treat 2 ml. of $NaNO_2$ test solution with dilute HCl. Account for the fumes which are evolved. Write the necessary equations.

2. Starch-Iodide Test for Nitrites. Hold in the escaping fumes from experiment 1 a strip of starch KI test paper. What change in color do you observe in the test paper? Account for this.

3. Ferrous Nitrosyl Test for Nitrites. Place 5 ml. of $NaNO_2$ in a test tube, add 5 ml. of dilute $HC_2H_3O_2$ and shake. Cool if the mixture feels warm. Then carefully and slowly add a few milliliters freshly prepared, concentrated $FeSO_4$ solution. Observe the color of the solution and write the reactions.

NITRATE, NO_3^-

With the parent substance, nitric acid, the student is already quite familiar. The reagent as usually dispensed in the laboratory is the constant boiling mixture of specific gravity 1.42, containing 68 per cent of pure nitric acid by weight. It is a strongly ionized acid and a vigorous oxidizing agent, which yields on reduction a series of products such as NO_2, NO, N_2O, N_2 and NH_3, depending upon the conditions of temperature, concentration and reducing agent present.

All normal nitrates are water soluble, but some on dissolving form insoluble basic salts by hydrolysis, for example, $BiONO_3$.

The most important reaction of nitrates from a qualitative standpoint is the so-called ring test, in which the nitrosyl ferrous complex, $Fe(NO)^{++}$, is formed. When concentrated H_2SO_4 is added to a nitrate, and then a strong solution of $FeSO_4$ is carefully added, reduction of the NO_3^- takes place, forming NO in accordance with the equation:

$$NO_3^- + 4H^+ + 3Fe^{++} = NO + 2H_2O + 3Fe^{+++}$$

As in the corresponding test for nitrites, the NO combines with Fe^{++} ion to form the $Fe(NO)^{++}$ complex:

$$Fe^{++} + NO = Fe(NO)^{++}$$

This appears as a dark brown ring at the junction of the two liquids. It is to be noted that nitrites must be removed, by decomposition with NH_4Cl or urea, since nitrites interfere by the formation of this complex. However, nitrites can be detected in the presence of nitrates since the test for the former can be made with acetic acid whereas the latter require concentrated sulfuric acid.

Nitron reagent is sometimes employed to detect nitrates. This reagent, which has the empirical formula $C_{20}H_{16}N_4$, forms in an acid solution an addition product $C_{20}H_{16}N_4 \cdot HNO_3$, a white crystalline substance. [The reagent is 1,4-diphenyl-3, 5-endanilo-dihydrotriazol and has the structural formula $C_6H_5-N-CH = (NC_6H_5)_2 = C = N$.] When dissolved in acetic acid, the reagent is known as "nitron," and when formic acid is used it is called "fornitrol." A number of other anions form insoluble products with the reagent. In systematic analysis, most of these are removed, including the nitrite.

Nitrates are reduced to ammonia by a number of metals, particularly aluminum and zinc, and this property may be utilized as a test for the nitrate ion. In the case of aluminum the reduction proceeds in an alkaline solution according to the equation:

$$8Al + 3NO_3^- + 5OH^- + 2H_2O = 8AlO_2^- + 3NH_3$$

The evolved ammonia is then tested for by litmus paper, as described on page 212. Ammonium salts must, of course, be absent from the solution of the sample when this test for nitrates is used.

PRELIMINARY EXPERIMENT

Ring Test for Nitrates. To 2 ml. of $NaNO_3$ test solution add an equal volume of concentrated H_2SO_4, mix and cool thoroughly under the water tap. Then, holding the test tube containing the cooled acidified test solution in an inclined position, carefully pour down the side of the tube a freshly prepared, concentrated solution of $FeSO_4$. Show by equations how the ferrous nitrosyl complex is formed.

REVIEW EXERCISES — SET 20

1. Write equations for the reactions involved in testing for (*a*) chlorates; (*b*) for the ester test (ethyl acetate) for acetates.

2. How can you test for a nitrite in the presence of a nitrite? After studying the following procedure tell how you would proceed with the detection of nitrate when nitrite has also been shown to be present in the same sample.

3. What is the apparent valence of chlorine in ClO_3^-, Cl^-, ClO_2^-, ClO^-?

4. Under what conditions will the nitrate ion act as an oxidizing agent? Write equations showing the function of NO_2^- as an oxidizer and as a reducer.

5. When dilute HNO_3 dissolves a metallic sulfide the NO_3^- becomes NO; when concentrated HNO_3 is employed as solvent for a metallic sulfide, the usual product is NO_2. Write balanced equations illustrating this for the action of dilute and concentrated HNO_3 on PbS.

6. The ionization constant of $HC_2H_3O_2$ is 1.8×10^{-5}. Would acetic acid be formed in a solution containing $NaC_2H_3O_2$ if an acid more weakly ionized than $HC_2H_3O_2$ were added? Explain why H_2SO_4 will liberate $HC_2H_3O_2$ from acetates.

7. If enough strong acid is added to a solution of $NaC_2H_3O_2$ to produce a molarity of 0.05 with respect to $HC_2H_3O_2$, what is the hydrogen-ion concentration in the test solutions which contains 10 milligrams per milliliter (10 grams per liter)?

8. The test solution of $NaC_2H_3O_2$ has undergone partial hydrolysis, because this salt is the product of the neutralization of a weak acid by a strong base. Calculate the hydroxyl-ion concentration in the test solution which contains 10 grams of $NaC_2H_3O_2$ per liter.

9. Predict the probable result on the precipitation of metallic sulfides in the cation procedures if acetate ions are present along with cations of Group II and III when adjustment of the acidity is made.

10. Give diagrammatic schemes for the separation and identification of the anions in the following mixtures:

(*a*) $SO_3^=$, $S^=$, CN^-, Cl^-, NO_3^-.
(*b*) AsO_2^-, ClO_3^-, $S^=$, I^-, $CrO_4^=$.
(*c*) $PO_4^{\equiv}$, $AsO_4^{\equiv}$, Cl^-, Br^-, NO_2^-, NO_3^-.

Outline of Method of Analysis of This Group

The chlorate, acetate and nitrite ions are identified in separate portions of the solution constituting this group. The chlorate is reduced to chloride ion and thus identified as AgCl. The acetate is here detected by the odor of one of its organic salts, namely ethyl acetate. The nitrite is tested for through the formation of the brownish colored ferrous nitrosyl complex, $Fe(NO)^{++}$, in an acetic acid solution.

The nitrate ion, however, in a systematic analysis, is sought in a portion of the original sample because, through the use of the

TABLE XIV

REACTIONS OF ANIONS

Anion($^-$)	$Ca(NO_3)_2$	$Ba(NO_3)_2$	$Zn(NO_3)_2$	$AgNO_3$ (Neutral)	Dilute HCl	Concentrated H_2SO_4
$CO_3^{=}$	$CaCO_3$ White	$BaCO_3$ white	$ZnCO_3$ white	$\underline{Ag_2CO_3}$ white changing to Ag_2O	$\overline{CO_2}$	$\overline{CO_2}$
$C_2O_4^{=}$	CaC_2O_4 White	BaC_2O_4 white		$Ag_2C_2O_4$ white		$\overline{CO} + \overline{CO_2}$
F^-	CaF_2 White	BaF_2 white	ZnF_2 white			$\overline{HF}$
BO_2^-	$Ca(BO_2)_2$ White	$Ba(BO_2)_2$ white		$AgBO_2$ white		$\overline{H_3BO_3}$
$SO_3^{=}$	$CaSO_3$ White	$BaSO_3$ white	$ZnSO_3$ white	Ag_2SO_3 white	$\overline{SO_2}$	$\overline{SO_2}$
AsO_2^-	$Ca(AsO_2)_2$ White	$Ba(AsO_2)_2$ white		Ag_3AsO_3 yellow		
$AsO_4^{\equiv}$	$Ca_3(AsO_4)_2$ White	$Ba_3(AsO_4)_2$ white		Ag_3AsO_4 chocolate		
$PO_4^{\equiv}$	$Ca_3(PO_4)_2$ White	$Ba_3(PO_4)_2$ white	$Zn_3(PO_4)_2$ white	Ag_3PO_4 yellow		
$C_4H_4O_6^{=}$	$CaC_4H_4O_6$ White	$BaC_4H_4O_6$ white		$Ag_2C_4H_4O_6$ white		$\overline{SO_2}$, CO_2 charring
$SO_4^{=}$		$BaSO_4$ white		Ag_2SO_4 white		
$CrO_4^{=}$		$BaCrO_4$ yellow		Ag_2CrO_4 red		

$S^{=}$			ZnS white	Ag_2S black	$\overline{H_2S}$	$\overline{H_2S} + \overline{SO_2}$
CN^-			$Zn(CN)_2$ white	$AgCN$ white	HCN	$\underline{CO}$
$Fe(CN)_6^{\equiv}$			$Zn_3K_2[Fe(CN)_6]_2$	$Ag_4Fe(CN)_6$ white		$\overline{CO}$
$Fe(CN)_6^{=}$			$Zn_3[Fe(CN)_6]_2$ yellow	$Ag_3Fe(CN)_6$ orange-red		$\overline{CO}$
$S_2O_3^{=}$				$Ag_2S_2O_3$ white	$\overline{SO_2} + \underline{S}$	$\overline{SO_2}$
CNS^-				$AgCNS$ white		
I^-				AgI yellow		
Br^-				$AgBr$ pale yellow		
Cl^-				$AgCl$ white		
ClO_3^-						
$C_2H_3O_2^-$						
NO_2^-				$AgNO_2$ in concentrated solution	$\overline{NO_2}$	$\overline{NO_2}$
NO_3^-						
$SiO_3^{=}$	$CaSiO_3$ White			Ag_2SiO_3 yellow		

group reagents, this ion will have been introduced into the solution. The so-called ring test, here employed, is interfered with by the presence of certain other anions. The removal of the interfering ions of other groups is carried out through their precipitation with barium acetate and silver acetate. Interfering chlorate is reduced and interfering nitrite eliminated by evaporation with NH_4Cl. In the resulting solution, the nitrate is then detected by the use of ferrous sulfate and concentrated H_2SO_4, producing the familiar " ring " of $Fe(NO)^{++}$.

Practice Analysis of a Mixture Containing Chlorate, Acetate, Nitrite and Nitrate Ions

Prepare a mixture containing 5 ml. of each of the test solution of $C_2H_3O_2^-$, ClO_3^-, NO_2^- and NO_3^-. Make the solution alkaline with 4 *M* NaOH. Use separate portions for the identification of each anion as described below.

Identification of Chlorate. The test for chlorates consists of reducing the chlorate to chloride and then following the procedure used previously for chlorides. Acidify 5 ml. of the test mixture with dilute H_2SO_4 and add 1 ml. in excess. Then add 0.1 to 0.2 of a gram of $NaNO_2$ to reduce the chlorate. Heat the solution to boiling. After boiling add 2 ml. of concentrated HNO_3 to destroy excess $NaNO_3$ and finally add 2 ml. of $AgNO_3$ reagent. The white precipitate is AgCl, which identifies chlorates in the original mixture.

Identification of Acetate. Take another 5-ml. portion of the test mixture, add 2 ml. of concentrated H_2SO_4, cool under the tap and add an equal volume of ethyl alcohol. Gently heat the mixture and note the fruity odor of ethyl acetate. The odor of ethyl alcohol must not be confused with that of the ethyl acetate.

Identification of Nitrite. To 5 ml. of the test mixture add acetic acid until neutral and then 5 ml. in excess. Shake the mixture and cool if necessary. Holding the test tube in an inclined position, carefully add 2 or 3 ml. of freshly prepared, saturated $FeSO_4$ solution. The brown color of the nitrosyl complex, $Fe(NO)^{++}$, identifies nitrites.

Identification of Nitrate. The " ring " test to be employed here in the analysis of this known mixture is interfered with by the presence of nitrite and chlorate. The former is destroyed by

evaporation with NH_4Cl and the latter by reduction with Na_2SO_3.

Place 5 ml. of the solution in an evaporating dish, add 3 to 4 grams of solid NH_4Cl and evaporate nearly to dryness. Add 10 ml. of water and repeat the evaporation. Again add 10 ml. of water, filter, discarding the residue if any.

To one half of the filtrate add dilute H_2SO_4 until acid and then 1 ml. in excess. Then add 0.1 of a gram of Na_2SO_3, heat to boiling, boil for one minute and filter. Cool the filtrate, add 5 ml. of concentrated H_2SO_4 and thoroughly cool in running water. Holding the test tube in an inclined position, carefully add several milliliters of freshly prepared ferrous sulfate solution. The brown ring which forms shows the presence of nitrate.

PART IV

SYSTEMATIC ANALYSIS

A complete qualitative chemical analysis of a sample of material consists of the separate systematic detection of cations and anions. The results will show not only which cations and anions are present but those that are absent as well. Within the scope of this book, as given in the systematic procedures, provision has been made for the study and detection of twenty-four of the commoner cations and an equal number of anions. In the case of a homogeneous substance such as a single salt, the positive detection of a single cation and of a single anion will usually identify the salt present. On the other hand, in a sample of greater complexity such as a mixture of salts, a qualitative analysis can usually only discover *which* ions are present and not how they may have been associated in the original mixture.

A complete systematic analysis involves (*a*) a preliminary examination of the sample, (*b*) the detection of anions and (*c*) the detection of cations, along with (*d*) an examination of the acid-insoluble residue. Since most of the anions interfere in one way or another with the cation analysis, it is advisable to complete the anion analysis before the cation detection is begun.

Types of Samples. In order to simplify the work and to keep the procedures from becoming too involved for the beginning student, the work outlined here provides for the analysis of samples of several different types, as follows:

1. Liquid samples, hereafter referred to as "test solution unknowns," composed of mixtures of cations of one or more cation groups or of mixtures of anions of one or several anion groups. This kind of student unknown is referred to again on page 277.
2. Solids consisting of a single compound. See page 278.
3. Solid mixtures of salts. This type of sample consists of unknowns made up of solid mixtures of several common salts. See page 280.

4. Alloys and metals. This type of unknown involves dissolving methods and analysis for cations and for a limited number of anions.

5. Ores, minerals and technical products. This type of sample will give some practice in fusion methods.

6. Silicates. The detection of silica in silicates by special methods is here considered.

SYSTEMATIC ANALYSIS OF "TEST SOLUTION UNKNOWNS"

These are the samples, submitted early in the laboratory course, which consist of mixtures of cations or of anions of a single group or combinations of several groups. They are usually made from the test solutions. The components are usually already in solution, hence no special provision need be made for dissolving the sample. Since the cation samples are derived mainly from the nitrates of the metals and the anion samples from the sodium or potassium salts, interferences are normally not encountered with this type of sample.

The procedures of analysis, already developed in Parts II and III, are incorporated in the schemes which follow, that for anion detection beginning on page 281 and that for cation detection beginning on page 290. The main consideration at this point is the preparation of the sample, so that detectable amounts of each ion may be present and the sample brought to a suitable volume.

Preparation of the Anion Solution. Since these samples consist of mixtures of anion test solutions of one or more groups, enough of the sample should be taken to insure the detection of all anions present. In general the anion tests are not as sensitive as those of the cations; for this reason it is best to provide for ample amounts of each anion. If the samples are compounded from the "stock" test solutions, each milliliter will contain 50 milligrams of anion. Take 10 ml. of the sample, add 2 ml. of 4 *M* NaOH if this has not already been done, dilute to 50 ml. with distilled water and proceed with the detection of the anions of Group I and of subsequent groups, depending upon whether the sample is one of a single group, a combination of several groups or a general anion sample comprising all groups. The procedure for Group I will be found on page 282.

Preparation of the Cation Solution. These samples are already in solution except as noted and are free from interfering anions, oxidizing agents and large concentrations of strong acids. In general the cation scheme is capable of detecting a few milligrams of any one cation in the presence of several hundred milligrams of other cations; hence, if the student sample was prepared from the dilute " 10-milligram-per-milliliter " student test solutions, a 25-ml. portion of the sample should be used. If, on the other hand, the " stock " test solutions were employed (100 milligrams per milliliter) it is best to dilute 10 ml. of the sample with 15 ml. of water, making a total volume of 25 ml. If a precipitate is present, the sample container should be shaken so that a proportionate part of the solid is included in the solution.

If the unknown is one in Group I alone, proceed with this 25-ml portion as directed in detail on page 295.

For Group II only see page 297; for Group III only, see page 303; for Group IV only, page 312; and Group V, page 313.

For unknowns of this type, covering all cation groups, or at least more than one group, take the 25-ml. portion and use the scheme beginning on page 295 for Group I and proceed through the cation groups.

In case the sample is submitted in the form of solid water-soluble nitrates and chlorides, dissolve a 1-gram portion in 25 ml. of water and proceed according to the several group precipitations.

SYSTEMATIC IDENTIFICATION OF A SINGLE SOLID COMPOUND

Samples composed of a single substance, usually a solid, are generally submitted for student analysis after the separate procedures for cation and anion analysis have been studied and " test solution unknowns " have been analyzed, but before the analyses of more complicated samples such as solid mixtures of salts, alloys, ores and technical products are undertaken. The sample may be a simple salt, an acid, a base or an oxide. In general, the procedure for the identification of the substance consists of a systematic search for the anion followed by that for the cation. A definite, pronounced test for an anion as well as that for a cation will identify the compound as a salt. If, however, an anion is definitely detected and no cation can be found the

conclusion is that the sample is an acid, the cation being the hydrogen ion. On the other hand, if a cation is found but no anion, the substance is either a hydroxide or an oxide.

In actually carrying out the procedures for the identification of the substance, a preliminary examination of the sample, as described on page 280, should be made first. The anion should be sought for next; then the cation should be identified.

Preparation of the Anion Solution. Whether or not the sample is water soluble, take 0.5 of a gram of the solid compound, add 25 ml. of molar Na_2CO_3 and boil for 5 minutes. Filter off the solid residue, add 2 ml. of 4 *M* NaOH to the filtrate, dilute to 50 ml. and proceed with the detection of the anion as described on page 282. This solution is referred to as the " prepared " solution.

Having identified the anion present, another portion of the sample is dissolved in water or acids and this solution is used for the detection of the cation.

Before the cation solution is made and the analysis is begun, the solubility relationships should be considered, since, because the anion present is known, some clues can be discovered regarding the cation likely to be present. For this purpose the solubility tables (on pages 330, 331 and 332) should be consulted. For example, suppose the sample is found to be a carbonate and the sample is water soluble; obviously, since the table shows all normal solid carbonates to be insoluble in water except Na_2CO_3 and K_2CO_3, the sample must be either one of these two. Or, again, suppose the sample is a water-insoluble sulfate; this fact limits the cation to lead or the alkaline earth elements. In this way, much help can be derived from the solubility table. The color of the compound should also be taken into consideration at this time.

There is likely to be no serious interference of anions with the cation procedure with these simple substances, and no special procedure except for phosphates, oxalates or tartrates need be introduced.

Preparation of the Cation Solution. The procedure for dissolving the sample depends upon the solubility of the sample.

1. If the sample is rather soluble in water, take a 0.5-gram portion, add 25 ml. of distilled water and heat to boiling. This will furnish a sufficient amount of the cation for its detection. Turn to the cation scheme on page 295 and follow the procedure until a decisive test is obtained.

2. If the sample is not appreciably soluble in water, treat a 0.5-gram portion of the sample with 5 ml. of dilute HNO_3, warming the mixture and adding more acid as long as action continues. If the sample has completely dissolved, evaporate the solution almost to dryness, dilute with 5 ml. of dilute HNO_3 and enough water to bring the volume to 25 ml. and proceed with the cation detection on page 295. If dilute HNO_3 fails to dissolve the sample completely, add 5 ml. of concentrated HNO_3 to the dilute HNO_3 used as original solvent, heat, and if no residue remains, evaporate and dilute as before.

3. If dilute or concentrated HNO_3 fails to dissolve the sample repeat, using dilute HCl and, if this fails, use aqua regia, in either case evaporating to small bulk in the presence of HNO_3, diluting to 25 ml. and using the resulting solution for the cation detection, as described on page 295.

SYSTEMATIC ANALYSIS OF MIXTURES OF SOLID SALTS

Preliminary Examination of Sample

A preliminary physical examination of the sample may throw considerable light on its nature and probable composition. Note the color and other physical properties. If possible, separate a small portion of the sample into its component salts, preferably by aid of a magnifying glass, and note the color, hardness, crystalline form, etc. If a physical separation is at all possible special tests on the separated portions may later be made to confirm the results of the systematic analyses.

Treat a small portion of the sample with hot water and note the color of the resulting solution or supernatant liquid; a colored solution may be due to the presence of water-soluble salts of copper, cobalt, nickel, iron or chromium, or to soluble chromates, dichromates, ferrocyanides or ferricyanides. Test the solution with litmus paper; an alkaline reaction will indicate a free base or salts which have hydrolyzed to give a basic solution, such as carbonates, sulfides, phosphates and borates; an acid reaction will indicate free acid, an acid salt or salts of heavy metals such as $FeCl_3$ which hydrolyze to give an acid solution.

Add dilute HCl to another small portion of the sample. If a gas is given off the possible presence of carbonates, sulfides, sul-

fites, cyanides, thiosulfates or nitrites will be revealed. *Be careful about smelling the gas if cyanides are likely to be present.*

Heating a portion of the sample in a hard glass tube is useful in revealing the presence of organic matter, though another test for organic matter is provided below.

Blowpipe tests, bead tests and the action of concentrated H_2SO_4 are sometimes resorted to in the preliminary examination, but the results are often hard for the beginner to interpret. The additional information secured is useful, however, in correlating the results of the systematic analysis.

Systematic Anion Analysis

In a complete systematic analysis of samples, especially of the kind under consideration, it is best to carry out the anion detection before that of the cations. With the exception of a few anions such as the carbonate and the nitrate in a dilute solution, most of the anions interfere with the regular scheme for the detection of the cations. By identifying the anions first, the proper steps can then be taken in preparing the solution for the cation analysis, introducing modifications in the regular scheme that will remove or otherwise overcome the interferences caused by the presence of these anions. The logical order, therefore, is to find out which anion or anions are present and what interference might result and then proceed with the preparation of the cation solution and its analysis; provision is also made, however, in the systematic cation procedure for the detection of cations independent of a prior anion analysis in cases where special emphasis is to be given to the cation content of the sample.

Preparation of the Anion Solution

In the procedure for the detection of anions the sample must be rendered soluble and, since most of the cations interfere, they must be removed. Acids cannot be used as solvents but Na_2CO_3 is used instead. The following instructions in regard to the treatment of the sample must be observed.

1. If the sample is a student unknown prepared from test solutions and intended for the detection of anions only, interfering cations will be absent, and the sample will be in solution or in

water-soluble form. Proceed with precipitation of Group I of the sample as described below.

2. If the sample is a solid compound or a mixture of salts and if it may contain cations other than sodium, potassium or ammonium, the sample must be treated with sodium carbonate. The solution so prepared is hereafter referred to as the " prepared " solution.

Take a 1-gram portion of the thoroughly mixed and powdered solid sample, add to it 25 ml. of molar Na_2CO_3 solution and boil for 5 minutes. Decant or filter off the supernatant liquid into a beaker and repeat the Na_2CO_3 treatment. Combine the solutions or filtrates for the anion analysis, reserving the residue for special tests.

This treatment will transpose the anions into soluble sodium salts and precipitate the cations as insoluble carbonates, basic carbonates or hydroxides. A few substances such as silicates, the halides of silver and certain phosphates are not transposed by mere boiling with Na_2CO_3. If these are suspected and not found by the regular procedure, the sodium carbonate residue should be examined for their presence.

Analysis of Group I

Group Precipitation. The procedure differs, depending upon whether chromates are present or absent. The reason is that, when chromates are present, boiling of the group precipitate is avoided in order to lessen the tendency of the chromate to oxidize reducing ions which may be present. The presence of chromates will be indicated by the yellow color of the " prepared " or original solution.

1. *In the absence of chromates,* (1) dilute the prepared solution (or original solution, in case it was unnecessary to prepare one) to 50 ml. (1) Add 2 ml. of 4 *M* sodium hydroxide and then add the group reagent, 1 *M* $Ca(NO_3)_2$ until precipitation is complete. Heat the mixture to boiling, allow to settle and filter. Wash the precipitate with 2 separate portions of water, adding the washings to the filtrate. Reserve the filtrate for subsequent boiling and analysis of subsequent groups.

Wash the residue repeatedly with small portions of water, until successive portions of the filtrate no longer give a test for the nitrate ion. This test is made to assure the complete removal of impurities from the residue. The " ring " test for the nitrate ion

is conducted by adding a small volume of concentrated H_2SO_4 to a few milliliters of the filtrate, cooling thoroughly and then adding a small volume of saturated $FeSO_4$ solution.

The precipitate will consist of the calcium salts of the anions of this group as well as some $Ca(OH)_2$.

2. *In the presence of chromates,* dilute the prepared or original solution to 50 ml. with water, add 2 ml. of 4 *M* sodium hydroxide and then 1 *M* $Ca(NO_3)_2$ solution until precipitation is complete.

Filter off the precipitate, saving the filtrate for further treatment and analysis of subsequent groups. Wash the precipitate with two 10-ml. portions of water, combining these washings with the main filtrate. Finally wash the residue with small portions of dilute NH_4OH until the yellow color of the chromate ion is no longer evident. Discard these latter washings.

The filtrate from either (1) or (2) should then be boiled to precipitate completely any sulfite ion left unprecipitated by the group reagent. If there is a precipitate, filter it off and add it to the main group precipitate. Use the filtrate for the analysis of Groups II through V.

Detection of Carbonate. If the "prepared" solution was used in the group precipitation, obviously $CaCO_3$ will be present in the group precipitate and the test for $CO_3^{=}$ must be made on a portion of the original sample. In this case proceed as follows: To a portion of the original sample in a test tube, add some solid $K_2Cr_2O_7$ (and 1 ml. of water if the sample is a solid) and then a few drops of dilute sulfuric acid. A vigorous effervescence is usually indicative of the presence of carbonates. This can be confirmed, if necessary, by the $Ba(OH)_2$ bead test described below.

If, on the other hand, the sample was not subjected to Na_2CO_3 treatment, the detection of carbonates is carried out as follows: Have at hand a platinum wire, in the loop of which is held a drop of $Ba(OH)_2$ reagent. Treat the group precipitate with 25 ml. of dilute (12.5 per cent) acetic acid, at the same time holding the drop of barium hydroxide in the escaping gas. If a vigorous effervescence takes place because of evolution of CO_2 and the drop of alkaline reagent turns turbid, the presence of carbonate is shown.

The residue, if one remains after the acetic acid treatment, may be CaC_2O_4 or CaF_2 or both. The acetic acid filtrate may contain borate, sulfite, arsenite, arsenate, phosphate and tartrate ions.

To proceed with the detection of the other ions of this group add 25 ml. of water to the acetic acid solution, filter off the precipitate if one remains and wash it repeatedly with small portions of water until separate portions of the washings no longer show a reducing action. The reducing test is made to remove the last traces of sulfite or arsenite which may remain in the precipitate. The reducing test is made by adding a drop of very dilute iodine solution, containing starch as indicator, to a small volume of the washings; the blue color of the test reagent will fade if reducing ions are present in the washings.

Detection of Oxalate. Treat the residue on the filter paper with 20 ml. of hot, dilute H_2SO_4 and wash once with 10 ml. of water. The filtrate from this may contain the oxalate ion. Take 5 ml. of this solution, heat it to boiling and add a few drops of 0.002 M $KMnO_4$ solution. A bleaching of the permanganate solution, due to reduction, shows the presence of the oxalate ion.

Detection of Fluoride. A residue remaining after the H_2SO_4 treatment is probably CaF_2. The etching test for fluorides is conducted as follows: Coat the bottom of a small watch glass with paraffin and make a scratch or some characters through the paraffin coating, in the central portion of the watch glass. Transfer the residue to a glass plate or slide, heap it up into a little cone and make a deep depression in the center. Place a few drops of concentrated H_2SO_4 in the crater, cover with the watch glass and set it aside. At the end of about a half-hour, examine the watch glass and note whether the glass where the surface was exposed by the scratch is etched by the hydrofluoric acid evolved from the calcium fluoride.

Detection of Borate. Take 2 ml. of the filtrate from the acetic acid treatment of the group precipitate and evaporate almost to dryness. Add a drop of concentrated HCl. Moisten a piece of turmeric paper with this solution, place it on a watch glass over a beaker of boiling water and allow the paper to dry. A pink coloration imparted to the paper shows the presence of borate. If no coloration results on the first drying, the test paper should be treated again as before. To make doubly sure, treat the spot with a drop of NaOH; the color should change to a dull green.

Detection of Sulfite. On a watch glass place a few drops of saturated $ZnSO_4$ solution, a drop or two of $K_4Fe(CN)_6$ solution,

together with several drops of sodium nitroprusside reagent. Then add a drop of the filtrate from the acetic acid treatment. A red color shows the presence of the sulfite ion.

To confirm this, take a small portion of the acetic acid filtrate and to it add 10 ml. of a hot, saturated solution of $HgCl_2$. If a sulfite is present, a white precipitate of Hg_2Cl_2 will form.

If sulfites are proved to be present boil 30 ml. of the acetic acid filtrate until free from sulfite, as shown by repeated tests for this ion. Bring the volume back to 30 ml. with water and divide into three portions.

Detection of Arsenite. To 5 ml. of the boiled filtrate, from which sulfite has been completely removed, add 5 ml. of water in order to reduce the acidity. Then add a few drops of starch solution and a few drops of 0.01 N iodine solution. The iodine will be reduced by the arsenite, with the disappearance of the blue color, if this anion is present.

Detection of Arsenate. To another 5 ml. portion of the boiled solution add 5 ml. of concentrated HCl and a small quantity of potassium iodide. The iodide ion will be oxidized by the arsenate ion to free iodine which gives a brown coloration to the solution, in case an arsenate is present.

Detection of Phosphate. If arsenate or arsenite are not present, test for the phosphate ion with $(NH_4)_2MoO_4$ as described below; if the interfering arsenic ions have been found, proceed as follows: Take 20 ml. of the boiled solution, add about 1 gram of sodium sulfite in order to reduce the arsenate to arsenite, make strongly acid by adding 2.5 ml. of concentrated HCl, heat to boiling and pass in hydrogen sulfide until precipitation of As_2S_3 is complete.

Filter off and discard the arsenious sulfide. Boil the filtrate to expel the excess of H_2S. The complete removal of H_2S should be tested for by holding over the boiling solution a strip of lead acetate paper, which in the presence of H_2S will become black. Hydrogen sulfide must be fully eliminated because if present, even in traces, it will reduce the ammonium molybdate reagent used in the phosphate test.

The filtrate, now free from arsenic and hydrogen sulfide, is then tested for phosphates. Add to 5 ml. of this an equal volume of water, 5 ml. of concentrated HNO_3, 1 gram of NH_4NO_3 and finally 10 ml. of ammonium molybdate solution. Heat this mixture

nearly to boiling. A yellow precipitate which may form is ammonium phospho-molybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$. This may stand 10 minutes before the precipitate forms.

Detection of Tartrate. Transfer the remainder of the solution to a small evaporating dish, evaporate nearly to dryness and then add a few drops of concentrated H_2SO_4. Charring accompanied by the odor of burnt sugar shows the presence of tartrates.

Analysis of Group II

To a small amount of the filtrate from Group I add a little $Ba(NO_3)_2$ reagent. The formation of a white or yellow precipitate shows the presence of this group. If this test is positive, carry out the separate test for sulfate and then the group precipitation.

Detection of Sulfate. To another small portion of the filtrate from Group I add dilute HCl until the solution is distinctly acid and then add the $Ba(NO_3)_2$ reagent. If a white precipitate forms here, it is $BaSO_4$ and proves the presence of sulfate.

Group Precipitation. To the remainder of the filtrate from Group I add $Ba(NO_3)_2$ until precipitation is complete. The precipitate may consist of $BaSO_4$ and $BaCrO_4$. A yellow color is positive proof of the presence of a chromate. Heat to boiling and filter off the precipitate, retaining the filtrate for the detection of ions of subsequent groups. Wash the precipitate until the washings no longer give a nitrate test.

Detection of Chromate. Treat the residue on the filter with dilute HCl, which will dissolve the $BaCrO_4$. Make the filtrate alkaline with dilute NH_4OH and then supply just enough dilute $HC_2H_3O_2$ to make the solution faintly acid. If chromate is present, yellow $BaCrO_4$ will again precipitate.

Analysis of Group III

Take a few milliliters of the filtrate from Group II and treat it with 5 ml. of 0.5 *M* zinc nitrate reagent. A precipitate shows the presence of members of this group. If a precipitate is formed, proceed as detailed below; if not, proceed with Group IV.

Group Precipitation. Treat the entire filtrate from Group II with 0.3 to 0.4 of a gram of solid Na_2CO_3 and, while stirring constantly, add the zinc nitrate until the precipitation is complete.

Filter. Reserve the filtrate for the analysis of subsequent groups. Wash the residue until separate small portions of the washings no longer give a test for the nitrate ion; discard the washings. Treat the group precipitate for the detection of sulfide, cyanide, ferrocyanide and ferricyanide according to the following procedures.

Detection of Sulfide. Divide the residue into two parts. To one part add a little water and shake to produce a suspension. Transfer a portion of the suspension to a test tube, moisten a strip of lead acetate test paper and, holding it over the mouth of the test tube, add a little dilute HCl to the tube. If the test paper turns brown or black, the presence of hydrogen sulfide is shown. The odor of H_2S will also be evident if considerable quantities of this gas are evolved, but do not deliberately attempt to detect H_2S by placing the nose near the test tube, since HCN will also be evolved if a cyanide is present.

Detection of Cyanide. Place another portion of the suspension in a small Erlenmeyer flask, add 5 ml. of water and then acidify with dilute HCl. Place over the mouth of the flask a piece of filter paper moistened with dilute NaOH. Heat the contents of the flask and boil for about a minute. Then treat the filter paper with 2 drops of freshly prepared $FeSO_4$ solution, acidify with one drop of concentrated HCl and finally one drop of $FeCl_3$ solution. The blue color which forms is Prussian blue, $Fe_4[Fe(CN)_6]_3$, precipitated by the ferrocyanide formed from the cyanide.

Detection of Ferrocyanide. To a portion of the residue, made slightly acid with dilute HCl, add a few drops of $FeCl_3$ reagent. Prussian blue will form if a ferrocyanide is present.

Detection of Ferricyanide. To still another portion of the suspension, add a few drops of freshly prepared $FeSO_4$. In the absence of ferrocyanides, if a blue precipitate (Turnbull's blue) forms, ferricyanides are shown to be present. The test is not entirely conclusive if the ferrocyanide ion is also present.

Analysis of Group IV

To 2 ml. of the filtrate from Group III, add a small volume of 5 per cent $AgNO_3$ and then make very faintly acid with dilute HNO_3. If a precipitate persists, members of this group are shown to be present; otherwise pass on to Group V.

Group Precipitation. If the precipitate formed in the preliminary test gradually darkens in color, the presence of the thiosulfate ion is shown. Owing to the hydrolysis of $Ag_2S_2O_3$ the solution may become acid enough to cause the reduction of the chlorate ion which may be present in the sample. To guard against this, if the presence of thiosulfate is indicated the filtrate from Group III should be made *just* alkaline by the careful addition of dilute NH_4OH; then 1 ml. in excess should be added. To this ammoniacal solution then add the $AgNO_3$ reagent until precipitation is complete, heat to boiling and finally add, dropwise, dilute HNO_3, with constant stirring. Allow the precipitate to settle, then filter and wash the precipitate twice with 10 ml. portions of water, adding these washings to the main filtrate. Reserve the filtrate for the detection of anions of Group V. Continue the washing of the group precipitate until free from $AgNO_3$; this is shown by testing successive portions of the washings with dilute HCl.

In case thiosulfates are not present omit the treatment with NH_4OH.

Detection of Thiosulfate. As already described, the test for the thiosulfate is made during the preliminary test as well as during the group precipitation. The detection is based on the fact that $Ag_2S_2O_3$ gradually undergoes decomposition into Ag_2S, with change in color from yellow through orange and red to black.

Detection of Thiocyanate. Remove a small part of the group precipitate, place it in a test tube, add 5 ml. of water and 5 ml. of $FeCl_3$ reagent. Shake the mixture and allow to settle. A deep red color imparted to the supernatant solution, due to the complex $Fe(CNS)_6^{\equiv}$ ion, shows the presence of the CNS^- ion.

Detection of Iodide. The halide ions now remain to be identified. In order to test for these, the silver salts must be put back into solution. This is accomplished as follows: Transfer the remainder of the group precipitate to a beaker, add 15 ml. of ammonium polysulfide and heat to boiling. This will dissolve the silver salts of these ions.

Acidify the solution with dilute H_2SO_4 in order to destroy the excess of polysulfide solvent. Heat to boiling to expel the hydrogen sulfide, filter off, wash twice and discard the residue, but retain the filtrate which now contains the halide ions.

To 5 ml. of this filtrate in a test tube, add NH_4OH until, as shown by litmus, the solution is faintly alkaline. Now add 2 ml.

of carbon tetrachloride and then, *drop by drop*, a solution of sodium hypochlorite. Shake the tube; if a violet color appears in the carbon tetrachloride layer it is due to iodine, liberated by the oxidation of the iodide ion by the NaOCl.

Detection of Bromide. To the same test tube in which the iodide test was made, add more NaOCl until the violet color is discharged and all the iodine has been oxidized to the colorless iodate form. Then acidify with dilute H_2SO_4 and continue treatment with NaOCl in order to oxidize the bromide ion to Br_2. A red or orange color in the carbon tetrachloride layer shows the presence of bromine.

Detection of Chloride. To another 5-ml. portion of the solution containing the dissolved halides, add $AgNO_3$ reagent until the precipitation of the silver salts is complete, heat to boiling and filter, discarding the filtrate. Wash the residue twice with 10 ml. of water.

Then treat the precipitate on the filter with 10 ml. of Miller's reagent (specially prepared NH_4OH containing $AgNO_3$ and KNO_3). This reagent will attack AgCl but not AgBr nor AgI.

The filtrate from this ammoniacal silver nitrate may contain the chloride in the form of $Ag(NH_3)_2^+$. To 1 ml. of this filtrate add enough dilute HNO_3 to acidify the solution. AgCl will be reprecipitated if chloride ion is present.

Analysis of Group V

The filtrate from Group IV will contain the excess of the group reagents added in the preceding procedures, namely, Ca^{++}, Ba^{++}, Zn^{++} and Ag^+ as well as Na^+ and NO_3^- ions. It may contain also chlorate, acetate and nitrite ions. In order to remove the cations added as group reagents, add solid Na_2CO_3 until a distinctly alkaline solution results, heat to boiling and evaporate to one-half the original volume, filter and wash once with a small volume of water.

Detection of Chlorate. To 4 or 5 ml. of this filtrate add dilute H_2SO_4 dropwise until acid to litmus and then 1 ml. in excess. Then add 0.2 of a gram of Na_2NO_3 to reduce the chlorate to chloride. Boil the solution, then add 2 ml. of concentrated HNO_3 to destroy excess $NaNO_2$ and finally add 2 ml. of $AgNO_3$. If a white precipitate (AgCl) forms it identifies chlorates in the original sample.

Detection of Acetate. Take another 5 ml. of the filtrate, add 2 ml. of concentrated H_2SO_4, cool under the tap and then add an equal volume of ethyl alcohol. Heat the mixture gently. The odor of ethyl acetate, if detected, identifies acetates in the sample.

Detection of Nitrite. To still another 5-ml. portion of the filtrate add dilute $HC_2H_3O_2$ until neutral and then acidify with 5 ml. more of the acetic acid. Shake the mixture, cooling if necessary. Then carefully add 2 or 3 ml. of freshly prepared, saturated $FeSO_4$ reagent. A brown color shows the presence of nitrite.

Detection of Nitrate. The test for nitrates must be made on a portion of the original or "prepared" solution, since nitrates have been added as group reagents. Furthermore, the "ring" test is interfered with by a number of ions. The removal of the anions of other groups is effected by the use of barium acetate and silver acetate; nitrites are removed by treatment with NH_4Cl and chlorates by reduction with Na_2SO_3. The detailed procedure follows.

To 10 ml. of the "prepared" solution or the same volume of the original sample, add a mixture of barium acetate and saturated silver acetate until precipitates no longer form. Heat the solution, filter and wash twice with 10 ml. of water, retaining the washings along with the filtrate. To the filtrate add 5 grams of solid NH_4Cl and evaporate almost to dryness. Add 10 ml. of water and again evaporate until only a few milliliters remain. Filter off and discard the residue.

To part of this filtrate add 2 ml. of concentrated H_2SO_4, and then 0.1 gram of solid Na_2SO_3, boil and filter. Cool the filtrate under the water tap. Incline the test tube and cautiously add several milliliters of freshly prepared $FeSO_4$ solution. A brown ring identifies nitrates in the original sample.

Systematic Cation Analysis

With samples consisting of mixtures of solid salts, where interfering anions, strong acids, oxidizing agents and organic matter may be present, special care must be taken in the preparation of the sample for the cation analysis and consideration must be given to the possibility of interferences. Before suitable means can be provided to correct for these interferences, we must know in what ways these objectionable substances interfere.

In a general way we can say that the difficulties encountered are of three kinds: (1) High concentrations of strong acids, especially the oxidizing acids, HNO_3 and aqua regia, as well as oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$ and $FeCl_3$, interfere by reacting with the H_2S used in the precipitation of sulfides and by producing colloidal or free sulfur or insoluble sulfates. (2) Anions of Groups I and II will, in a neutral or basic solution, precipitate insoluble salts if Ca^{++}, Ba^{++}, Sr^{++} or Mg^{++} (and possibly Pb^{++}) are present and this will make detection of these cations uncertain or even impossible unless modifications are introduced. (3) The formation of complex ions with certain anions and cations may prevent the precipitation of the cations in question. In addition, certain anions interfere with the regulation of the sulfide-ion concentration, produce insoluble compounds or otherwise obstruct the simple operation of the regular scheme of analysis.

Before the specific interference of the individual anions is discussed, it may be well to state at this point that there is a general method applicable to the removal of many of these troublesome substances. This consists of volatilizing or destroying them by fuming down the solution with H_2SO_4. The details of this method are described later. In certain cases there is a simpler way out of the difficulty, but the method nevertheless must be employed for the removal of certain objectionable substances and, moreover, if for any reason the anion analysis has not yet been made, the treatment with H_2SO_4 must be resorted to.

The chief causes of difficulty, together with a hint for overcoming the interference, are here briefly enumerated, listing the anions in the order of the systematic anion scheme.

Carbonates. Carbonates do not interfere. They will be evolved as CO_2 during acid treatment in dissolving the sample or during precipitation of Group I.

Oxalates. Oxalates cause the premature precipitation of Ca^{++}, Sr^{++}, Ba^{++} and Mg^{++} in Group III. They can be removed by the general fuming-down method or by the special method described on page 309.

Fluorides. Fluorides interfere the same as oxalates. They can be removed as HF by fuming down with H_2SO_4.

Borates. Borates interfere the same as oxalates and are volatilized as boric acid with H_2SO_4.

Sulfites. Sulfites will react with H_2S to produce free or colloidal sulfur in Group II. They can be removed by acid treatment.

Arsenites. There is no interference. Arsenites are precipitated as As_2S_3 in Group II according to regular procedure.

Arsenates. Arsenates are slowly and possible incompletely precipitated in Group II unless reduced with NH_4I according to the regular procedure.

Phosphates. There is serious interference since Ca^{++}, Sr^{++}, Ba^{++} and Mg^{++} will be precipitated in Group III. In the presence of phosphates, the modification of the procedure described on page 310 must be used.

Tartrates. Tartrates interfere in same way as oxalates and phosphates. Besides, the tartrate ion forms complexes with Al and Cr, preventing precipitation of these cations. They can be removed by fuming down according to (*a*) the general method or (*b*) as described on page 309.

Sulfates. Sulfates will cause precipitation of $BaSO_4$, $SrSO_4$, $PbSO_4$ and possibly $CaSO_4$. These cations are then sought for in the acid-insoluble residue according to the procedure given on page 315.

Chromates. Chromates interfere by oxidizing the hydrogen sulfide in Group II. They are reduced with alcohol or H_2SO_3. The Cr^{+++} is then detected in Group III.

Sulfides. In dissolving the sample in HNO_3, sulfides may produce free sulfur or SO_4 ions. For sulfides soluble in HCl the difficulty is easily overcome but for the nitric acid-soluble sulfides, interference is unavoidable.

Cyanides. Cyanides may form stable complex ions with elements like copper and thus prevent precipitation of sulfides. Should be avoided in student samples on account of their poisonous nature. Treatment with acids will decompose cyanides with liberation of HCN.

Ferrocyanides and Ferricyanides. The tendency to react with each other and to form insoluble and difficultly filtrable products lead to considerable trouble. The general method of treatment with concentrated H_2SO_4 will decompose salts of these complex cyanides.

Thiosulfates. Same as sulfites.

Thiocyanates. In presence of iron thiocyanates produce color interference. They can be removed by acid treatment.

Iodides. Iodides will precipitate Ag, Pb and Hg (ous) as acid-

insoluble salts. They are easily oxidized by nitric acid with liberation of free iodine. They can be removed by treatment with concentrated H_2SO_4.

Bromides. Same as iodides.

Chlorides. Same as iodides except that chlorine is not liberated with nitric acid.

Chlorates. Chlorates may cause oxidation, in an acid solution, of reducing substances such as the halides, and nitrites. They will oxidize H_2S to sulfur. They can be removed by treatment with H_2SO_3. It should be remembered that a violently explosive mixture is produced when a solid chlorate is warmed with concentrated H_2SO_4.

Acetates. Acetates interfere with the regulation of the hydrogen-ion and sulfide-ion concentrations during precipitation of Group II. They can be easily removed by boiling with an acid.

Nitrites. Nitrites will oxidize H_2S. They can be removed by acid treatment.

Nitrates. There is no interference when nitrates are present in dilute solution but they oxidize H_2S when present as strong HNO_3. They can be removed by fuming down with H_2SO_4.

Silicates. Decomposable silicates would precipitate as silicic acid in Group I. They can be removed as described on page 310.

Organic Matter. Substances like sugar, starch and organic compounds of like nature interfere much as do tartrates and are removed by similar methods.

The means of removing these interfering substances can be summarized as follows:

1. By volatilization with acids without drastic fuming down: $CO_3^{=}$, BO_2^{-}, $SO_3^{=}$, $S^{=}$, CN^{-}, $S_2O_3^{=}$, CNS^{-}, $C_2H_3O_2^{-}$, NO_2^{-}.

2. By fuming down with HNO_3 and concentrated H_2SO_4: $C_2O_4^{=}$, F^{-}, $C_4H_4O_6^{=}$, $Fe(CN)_6^{\equiv\equiv}$, $Fe(CN)_6^{\equiv}$, I^{-}, Br^{-}, Cl^{-}, organic matter, NO_3^{-}.

3. By reduction with H_2SO_3: $CrO_4^{=}$, ClO_3^{-}, $AsO_4^{\equiv}$, (MnO_4^{-}).

4. By special methods: $PO_4^{\equiv}$. See page 310; for special procedure for $C_2O_4^{=}$ and $C_4H_4O_6^{=}$ see page 309.

Preparation of the Cation Solution

The treatment of the sample, in getting it into solution and removing the interfering substances, may be varied somewhat

depending upon the solubility of the sample and what anions are present.

1. If the sample is readily soluble in dilute HNO_3 (as shown by a trial) and free from anions which require fuming down, treat a 1-gram portion with 25 ml. of dilute HNO_3, boil until completely dissolved, bring the volume to 25 ml. and proceed with the precipitation of Group I.

2. If interfering anions of other types are present proceed as follows: Treat a 1-gram portion of sample in an evaporating dish with 15 ml. of dilute H_2SO_4 and 5 ml. of concentrated HNO_3. Boil the mixture until SO_3 fumes are evolved. Add 10 ml. more of HNO_3 and again fume down to SO_3 fumes. If tartrates are present and the solution still retains a deep brown color, repeat the acid treatment.

This treatment should destroy oxalates, tartrates and organic matter as well as ferrocyanides and ferricyanides, decompose carbonates, cyanides and other volatile acids, and render soluble most of the insoluble combinations.

Comparatively few compounds are insoluble in strong HNO_3, hence this acid is the best solvent. It will, however, transform salts of antimony and tin into insoluble Sb_2O_5 and $SnO_2 \cdot H_2O$, which, however, are dissolved by HCl. Nitric acid will oxidize mercurous, ferrous, stannous, arsenious and antimonous compounds, and change sulfides to sulfur or to sulfuric acid with the consequent precipitation of free sulfur or of sulfates of lead, barium, strontium and calcium. Silicic acid may be precipitated as a gelatinous residue during the treatment with nitric acid.

Dilute the acid solution to 25 ml. with water and use the filtrate for the cation analysis unless a residue remains.

3. If a residue remains insoluble in concentrated HNO_3 treat it with 5 ml. of concentrated HCl and heat until action ceases. Add a few milliliters of concentrated HNO_3 if a residue still remains, thus making aqua regia the solvent; heat, dilute and filter. Unite this filtrate with the solutions obtained from the HNO_3 treatments and follow the procedure outlined below for the analysis of the cations.

The residue resisting the action of all acids is referred to as the "acid-insoluble residue" and must be examined by the methods given under "Analysis of the Insoluble Residue," page 315.

Note: If the sample is a "test solution unknown" known to contain ions of Group I alone, a 25-ml. portion will already have been prepared as directed on page 278, and the group precipitation and analysis can be carried out directly as described below.

If the sample is of the same type as the above but is known to contain ions of other groups as well, the 25-ml. portion, already prepared as described on page 278, is analyzed by the procedures beginning with Group I. The presence of a precipitate indicates either that a chloride along with Ag^+, Hg_2^{++} or Pb^{++} reacted to form $AgCl$, Hg_2Cl_2 or $PbCl_2$ or else oxychlorides or oxynitrates of Bi, Sb or Sn are present. In either case the analysis of the mixture will reveal the composition of the precipitate.

If the sample is a single solid compound, the cation solution will have been prepared as described on page 279. Proceed with the precipitation of Group I.

Analysis of Group I

Group Precipitation. Take the 25-ml. portion of the solution just prepared and add dilute HCl slowly with constant stirring until a precipitate no longer forms. Allow the precipitate to settle and to the clear supernatant liquid add a drop or two of dilute HCl; if incomplete precipitation is indicated by the formation of a white precipitate, continue the addition of HCl until precipitation is complete; then add about 1 ml. more of HCl. Any basic salts of bismuth or antimony formed on dilution will dissolve in this concentration of HCl. The precipitate may consist of $AgCl$, Hg_2Cl_2 and $PbCl_2$. If lead is present in very small amount, it may escape precipitation here; in this case it will be found in the next group.

Pour off the supernatant liquid through a filter. Wash the precipitate in the beaker first with dilute HCl to prevent the precipitation of $BiOCl$ and $SbOCl$ and then several times with small portions of water, decanting through the filter each time. The filtrate may contain ions of subsequent groups, unprecipitated lead and excess HCl; set it aside in a labeled, stoppered Erlenmeyer for subsequent analysis.

Detection of Lead. Boil the Group I precipitate in the beaker with 5 ml. of water and then transfer the solution and residue to a filter paper, flushing with a few milliliters of hot water and

catching the filtrate in a test tube. If a residue remains, which may be either AgCl or Hg_2Cl_2 or both, wash it several times with the hot filtrate by pouring it over the residue.

The hot water filtrate may contain dissolved $PbCl_2$; needle-like crystals of lead chloride may crystallize out when the filtrate is cooled. This filtrate is tested for lead as follows:

To a few milliliters of the filtrate add a few drops of K_2CrO_4 reagent. A yellow precipitate of $PbCrO_4$ shows the presence of lead.

Confirm this by adding to another small portion of the filtrate a few drops of dilute H_2SO_4. A white crystalline precipitate of $PbSO_4$ further confirms the presence of lead.

Detection of Silver. If a white residue remains after the hot water treatment of the group precipitate, it indicates the presence of either silver or mercurous mercury or both. If lead was found present, wash this residue on the filter paper repeatedly with small portions of hot water until the washings no longer give a test for lead; otherwise, omit this washing step.

Then pour over the residue a few milliliters of dilute NH_4OH, receiving the filtrate in a clean test tube. A turbid filtrate here may be due to basic lead chloride, PbOHCl, formed through the action of ammonia on unextracted lead chloride. This will dissolve in HNO_3 and will not interfere with the test for silver.

Acidify the filtrate with dilute HNO_3, shaking the tube and testing with litmus paper. A curdy, white precipitate of AgCl shows the presence of silver in the sample.

A blackening of the residue during the ammonia treatment indicates the presence of mercury. If the amount of mercury is large and that of AgCl is small the AgCl may be reduced to metallic silver, according to the reaction $2AgCl + 2Hg = 2Ag + Hg_2Cl_2$, and thus escape detection. If silver is not found by the above test, carry out the confirmatory test for mercury as directed below and treat the thoroughly washed residue remaining undissolved by the aqua regia with dilute NH_4OH and then acidify with dilute HNO_3. If small amounts of silver are present a white precipitate of AgCl will form.

Detection of Mercury. If on treating the residue remaining from the hot water treatment with dilute NH_4OH the residue turns black, it is a strong indication that mercury is present. The black residue consists of metallic mercury and $HgNH_2Cl$. Should

such a black residue remain after the ammonia treatment, dissolve it in aqua regia. This may be done by punching a hole in the bottom of the filter and pouring a few milliliters of aqua regia through the funnel, catching the residue and liquid in a small evaporating dish; or, if the residue is large, transfer it to the dish by means of a porcelain spatula and add 2 ml. of aqua regia. Heat until the black color clears up, boil to destroy excess aqua regia or chlorine, dilute to 5 ml. and filter if necessary. (A white residue at this point will be AgCl and is identified as previously directed.) To the filtrate add a few drops of $SnCl_2$ solution. A white precipitate turning gray or black proves the presence of mercury.

Analysis of Group II

The solution, which may be the filtrate from Group I or an unknown mixture of this group only, must be freed from objectionable constituents and brought to the proper acidity before precipitation with H_2S. The principal objectionable constituents are large amounts of strong acids and oxidizing agents. These interfere, first, by oxidizing the H_2S to free sulfur or to sulfuric acid, masking the results and causing the precipitation of insoluble sulfates of Group IV, and second, by causing difficulties in the regulation of the acidity by which the sulfide-ion concentration is controlled.

1. If strong acids are known to be absent, make the solution faintly basic with NH_4OH and then just acid with dilute HCl, testing the solution with litmus paper during the addition of the NH_4OH and HCl. Add exactly 2.5 ml. of concentrated HCl and dilute the volume to exactly 50 ml. with distilled water. Disregard any precipitates which may form during the ammonium hydroxide addition or during dilution, since these will dissolve or be changed into sulfides on treatment with H_2S.

2. If strong acids, particularly HNO_3, are known to be present (and the excess is not removed by the method already prescribed) or, if the concentration of acid is known to be in excess of that required for precipitation of this group (2.5 ml. of concentrated HCl), add 5 ml. of concentrated HNO_3 and evaporate the solution almost to dryness, but do not bake the residue. Add about 1 ml. of concentrated HCl and again evaporate almost to dryness. Add 20 ml. of water, stirring the pasty mass until it dissolves.

Neutralize with dilute NH_4OH and then add 2.5 ml. of concentrated HCl. Make up the volume of this solution to exactly 50 ml. with distilled water. This treatment removes the strong oxidizing acids, destroys acetates and organic matter and converts $AsCl_3$ and $HgCl_2$ into non-volatile compounds.

Group Precipitation. To the solution as prepared above, add 1 ml. of NH_4I, heat nearly to boiling and pass into the hot solution a rapid stream of H_2S for at least 5 minutes. Without filtering, add 50 ml. of cold water, making the volume 100 ml., thoroughly cool in running water and again pass in H_2S for from 5 to 10 minutes. Filter and pass H_2S into the filtrate to ascertain whether precipitation is complete; if a precipitate forms continue the treatment with H_2S until precipitation is complete. Allow the precipitated sulfides to settle and filter through the same filter. If the solution filters through cloudy, because of the presence of colloidal sulfur or colloidal sulfides, add a little NH_4NO_3 solution to the filtrate and refilter. Boil the filtrate until the odor of H_2S is no longer noticeable and set it aside in a stoppered Erlenmeyer for the analysis of subsequent groups.

Wash the precipitate on the filter with small portions of water containing H_2S and a small quantity of NH_4NO_3 until the washings give only a faint acid reaction with litmus paper. The precipitate may consist of HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3 (As_2S_5), Sb_2S_3, Sb_2S_5, SnS and SnS_2. Some free sulfur will always be present.

Note the color of the precipitate and draw conclusions as to the sulfides likely to be present.

If the precipitate is white and finely divided or the solution is merely rendered turbid during treatment with H_2S, only sulfur is likely to be present; in this case proceed with the analysis of the filtrate for Group III as described on page 303.

Separation into Divisions A and B. Transfer the well-washed group precipitate to a small beaker or evaporating dish, add 10 ml. of $(NH_4)_2S_2$, stir and warm. Add 10 ml. of water and filter. Repeat the extraction with a few milliliters of $(NH_4)_2S_2$, add a few milliliters of water, filter and test a small portion of this second filtrate for complete extraction by acidifying it with dilute HCl. No orange or yellow precipitate will form in this acidified portion other than a slight turbidity or finely divided white precipitate of free sulfur if the extraction is complete. In case of

incomplete separation, repeat the $(NH_4)_2S_2$ treatment with small portions of the solvent until tests on separate, fresh portions of the filtrate give no yellow or orange precipitate.

Unite the filtrates for the analysis of Division B. Wash the residue at least twice with small portions of hot wash water containing NH_4NO_3 and analyze for members of Division A.

The above treatment with $(NH_4)_2S_2$ dissolves the sulfides of arsenic, antimony and tin, oxidizing at the same time those of lower valence to the higher state of oxidation, and leaving undissolved the sulfides of mercury, lead, bismuth, cadmium and most of the copper. A white precipitate of sulfur left after the extraction should not be mistaken for Division A. A small amount of CuS will dissolve in the reagent. The members of Division B are now in solution as $AsS_4^{\equiv}$, $SbS_4^{\equiv}$ and $SnS_3^{=}$.

Analysis of Division A — The Copper Subgroup. The residue, if there is one, from the ammonium polysulfide treatment may be composed of HgS, PbS, Bi_2S_3, CuS and CdS. Transfer it to a beaker, add 20 ml. of 1:7 HNO_3, heat for several minutes while stirring constantly and filter. Save the filtrate for the analysis of the other members of this subgroup.

A residue remaining may be HgS or a double salt such as $2HgS \cdot Hg(NO_3)_2$ or gummy sulfur, and possibly a little $PbSO_4$, resulting from the oxidation of PbS by the HNO_3, though not enough to interfere with the tests for mercury and lead.

Detection of Mercury. Wash the residue, if there is one, with water, transfer it to a beaker and boil with 5 ml. of aqua regia until brown fumes of NO_2 are no longer evolved and all chlorine is expelled. Do not evaporate to dryness. Dilute with a few milliliters of water and filter. To the filtrate add a few drops of $SnCl_2$ reagent. A white precipitate or cloudy solution turning gray or black shows the presence of mercury.

Detection of Lead. The filtrate from the separation of mercury may contain Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++} ions and excess HNO_3. Place the filtrate in an evaporating dish, add 5 ml. of concentrated H_2SO_4 and evaporate under the hood until white, cloudy fumes of SO_3 appear. This will not occur until all the HNO_3 has been evolved and the volume has been reduced to a few milliliters. It is important that all HNO_3 be removed because $PbSO_4$ is somewhat soluble in this acid and its presence in the filtrate will interfere with the test for bismuth.

Cool the solution and pour it slowly into 20 ml. of water, wash the dish with a few milliliters of water, adding this to the solution; allow the mixture to settle and then filter. Reserve this filtrate for tests for Bi^{+++}, Cu^{++} and Cd^{++}. A white, finely crystalline precipitate, $PbSO_4$, is a good indication of lead. Basic bismuth sulfate, $(BiO)_2SO_4$, may appear at this point and be mistaken for $PbSO_4$; hence a confirmatory test for lead should be made.

Wash the white precipitate with a little water and then pour through the filter 10 ml. of hot $NH_4C_2H_3O_2$ solution. Reheat the filtrate and repeat the extraction. Add a few milliliters of acetic acid and several drops of K_2CrO_4 to the filtrate. A yellow precipitate of $PbCrO_4$ confirms the presence of lead.

Detection of Bismuth. Neutralize the filtrate from the lead separation with dilute NH_4OH, and then add a few milliliters in excess in order to dissolve copper and cadmium hydroxides if present. A white precipitate remaining is $Bi(OH)_3$. If copper is present, it will be evidenced at this point by an intense blue coloration in the solution. Confirm the presence of bismuth as follows:

Filter off the white precipitate and wash with water. Remove and dissolve a portion in a few drops of dilute HCl and pour the solution into about 50 ml. of warm water. A white precipitate or turbidity is due to BiOCl. If the acid concentration is too high the test may fail; before discarding the test as negative, carefully add dilute NH_4OH until the excess of acid is neutralized, allow to stand several minutes and note whether a precipitate forms.

The best test for bismuth is carried out as follows: Prepare fresh sodium stannite, Na_2SnO_2, by adding NaOH to a few milliliters of $SnCl_2$ solution until the precipitate, which first forms, dissolves. Cool the reagent and add a few drops to the $Bi(OH)_3$ remaining on the filter paper. The precipitate will turn black if bismuth is present.

Detection of Copper. A deep blue solution obtained during the $Bi(OH)_3$ separation, which is due to the complex copper-ammonia ion, $Cu(NH_3)_4^{++}$, is usually sufficient proof of the presence of copper (see note under arsenic test, page 302).

For traces of copper, the test with potassium ferrocyanide, $K_4Fe(CN)_6$, is more sensitive. To carry out this test, take a

small portion of the solution, make it slightly acid with H_2SO_4 and add a few drops of dilute $K_4Fe(CN)_6$ solution. A reddish brown color due to $Cu_2Fe(CN)_6$ confirms the presence of copper. Care must be taken not to add an excess of the reagent, otherwise white $Cd_2Fe(CN)_6$ will form if cadmium is present.

Detection of Cadmium. In the absence of copper, make the colorless filtrate from the bismuth separation faintly acid with dilute H_2SO_4 and pass in H_2S. A yellow precipitate of CdS shows the presence of cadmium.

If the precipitate is dark colored, owing to small amounts of HgS and PbS, boil the residue for several minutes with $1:4H_2SO_4$. Only CdS will dissolve in this concentration of acid. Dilute the filtrate with about 50 ml. of water and reprecipitate the CdS with H_2S.

In the presence of copper, the use of KCN is resorted to, in order to test for cadmium. In carrying out this test *use utmost care with KCN, since this reagent is a violent poison. Carry out the test under the hood.* Proceed as follows:

Add KCN to the deep blue solution until the color is discharged and the precipitate which first forms dissolves in the excess of reagent. Then saturate the solution with H_2S. Under these conditions copper does not precipitate but cadmium does as yellow CdS. If this sulfide precipitate is dark colored, treat it with 3 ml. of 1:4 H_2SO_4, filter, dilute the filtrate to about 50 ml. and pass in H_2S. A yellow precipitate shows the presence of cadmium. See the preliminary experiments with KCN (page 144) for an explanation of the above test for cadmium in the presence of copper.

Analysis of Division B — The Tin Subgroup. The filtrate from the ammonium polysulfide treatment may contain arsenic as $AsS_4^{\equiv}$, antimony as $SbS_4^{\equiv}$ and tin as $SnS_3^{=}$, together with an excess of $(NH_4)_2S_2$.

Add enough dilute HCl to just acidify the solution. Avoid an excess, because SnS_2 is somewhat soluble in dilute acid. As_2S_5, Sb_2S_5 and SnS_2 will precipitate if these metals are present. Traces of CuS or HgS may give the precipitate a dark color. A yellow, turbid solution may be due to colloidal sulfur.

Filter and wash the precipitate, discarding the filtrate.

➤**Separation and Detection of Arsenic.** Transfer the precipitate to a 100-ml. beaker, add 10 ml. of concentrated HCl and bring the mixture almost to boiling, stirring it vigorously for several min-

utes. As_2S_5 is relatively insoluble in concentrated HCl whereas Sb_2S_5 and SnS_2 readily dissolve. Do not allow the solution to boil, as there is danger of dissolving As_2S_5 with loss of volatile $AsCl_3$ according to the reversible reaction: $As_2S_5 + 10HCl \rightleftharpoons 2AsCl_5 + 5H_2S$. Some Sb_2S_5 may remain undissolved and give an orange color to the residue but its presence will not interfere with the test for arsenic.

Dilute with 5 ml. of water and filter. Reserve the filtrate for tests for antimony and tin.

Treat the residue with 5 ml. of concentrated HNO_3, warming until brown fumes are no longer evolved and only a residue of gummy sulfur remains. The HNO_3 converts the As_2S_5 into H_3AsO_4. Filter, divide the filtrate into three parts and to the first add 2 ml. of magnesia mixture ($MgCl_2$, NH_4OH and NH_4Cl). Make the solution strongly ammoniacal with concentrated NH_4OH, shake and allow the solution to stand for some time. Before rejecting the test as negative, rub the sides of the test tube with a glass rod to hasten precipitation. A white, crystalline precipitate of $MgNH_4AsO_4$ shows the presence of arsenic.

If, during the addition of magnesia mixture or in making the solution ammoniacal, the solution develops a deep blue color, the presence of copper is indicated. CuS is somewhat soluble in $(NH_4)_2S_2$ and if only traces of copper are present in the sample, the copper test may have been missed (see page 300); in this case the presence of copper will be revealed here.

To the second part of the arsenate solution, add NH_4OH to neutralize the HNO_3; then just acidify with $HC_2H_3O_2$ and add dilute $AgNO_3$. A chocolate brown color due to Ag_3AsO_4 shows arsenic. The acetic acid serves to neutralize the last traces of NH_4OH which, if present, might form Ag_2O and would dissolve Ag_3AsO_4.

To the third portion reserved for the detection of arsenic, add 2 ml. of ammonium molybdate and warm the mixture. If a yellow precipitate forms after standing for some time, arsenic is shown to be present.

Detection of Antimony. Dilute the filtrate from the As_2S_5 separation to exactly 50 ml., heat almost to boiling and pass in H_2S for 10 minutes. If antimony is present an orange precipitate of Sb_2S_3 will form. If precautions are not taken, SnS_2 may partially precipitate and traces of CuS and HgS may discolor the precipitate.

To confirm the presence of antimony filter and dissolve the precipitate in 2 ml. of concentrated HCl, dilute and divide the solution into two approximately equal parts.

To one portion add a few pieces of aluminum foil and warm. The black deposit is metallic antimony. Prove this still further by decanting off the solution and showing that the black deposit is insoluble in sodium hypochlorite, NaOCl.

To 1 ml. of the other portion of antimony trichloride solution, add some crystals of KNO_2 in order to oxidize the antimony to the pentavalent state. After effervescence has ceased, add several drops of rhodamine-B reagent. The change in color from bright red to violet is due to the presence of antimony.

Detection of Tin. Evaporate the filtrate from the removal of Sb_2S_3 to 25 ml.; boil off the H_2S. To part of this add an iron nail, evaporate to small volume and filter at once into a test tube containing $HgCl_2$ reagent. A white precipitate of Hg_2Cl_2 turning gray or black shows the presence of tin. In place of an iron nail, a short length of aluminum wire may be used, the solution made acidic with HCl, boiled to dissolve any metallic tin which may separate and then filtered into $HgCl_2$ solution.

To another portion in a watch glass or small dish add a piece of metallic zinc. Place some cold water in a crucible and, with crucible tongs, immerse the bottom of the crucible in the solution being tested. Hold the crucible in a flame, and observe the intense bluish color of the flame along the margin of the unglazed bottom of the crucible.

Analysis of Group III

The presence of phosphates, oxalates and tartrates or similar organic material will interfere with the detection of the cations of this group and Group IV. Accordingly, these anions must be tested, unless this has already been done by a complete anion analysis of another portion of the original sample. If found present, modifications must be made in the regular procedure to remove them or otherwise to overcome the interference.

Therefore, carefully observe the following instructions:

1. If the sample is a " test solution unknown " of members of this group only, or a general cation sample containing members of preceding and following groups or, in fact, any sample definitely

known not to contain phosphates, oxalates or tartrates, proceed directly with the " Procedure — Absence of Interfering Anions."

2. If, on the other hand, these interfering anions are suspected of being present and are to be tested for, or the sample is submitted for the express purpose of following the modified procedure, use the " Procedure — Presence of Interfering Anions."

Procedure — Absence of Interfering Anions

The procedure outlined below applies only in the absence of phosphates, oxalates, tartrates and other interfering anions. Unless these substances are known to be absent or have already been tested for, they should be tested for by the methods given on page 308.

The sample for analysis may be a mixture of this group only or it may be the filtrate from Group II. A colored solution will indicate the presence of nickel, cobalt, ferric iron or chromium; colorless solutions may contain manganese, ferrous iron, aluminum or zinc. If chromates, dichromates or permanganates are present in a general unknown, these anions will have been changed to green chromic or colorless manganous ions prior to or during the precipitation of Group II.

Group Precipitation. Add about 2 grams of solid NH_4Cl, make the solution ammoniacal with dilute NH_4OH and then add an excess of 2 ml. of concentrated NH_4OH. Heat the solution almost to boiling and pass into it a stream of H_2S. A precipitate will form if members of this group are present; otherwise, treat the solution as described below and then pass on directly to the procedure for Group IV as directed on page 312.

Filter a small portion and test the filtrate with H_2S for complete precipitation. When precipitation is complete filter through a fluted filter by means of which a more rapid filtration is possible. Wash the precipitated sulfides and hydroxides with hot water containing a small quantity of NH_4Cl. If the filtrate is to be analyzed for Groups IV and V, acidify it at once with dilute acetic acid, boil to expel H_2S, filter if not clear and set aside in a stoppered Erlenmeyer.

The addition of NH_4Cl to the solution before precipitation is important for several reasons. It (1) prevents the precipitation of magnesium as $Mg(OH)_2$ in this group; (2) it decreases the

solubility of $Al(OH)_3$ and $Cr(OH)_3$, and (3) it lessens the tendency toward the formation of colloidal sulfides.

The net effect of the group reagent is to precipitate NiS, CoS, MnS, FeS, Fe_2S_3, ZnS, $Al(OH)_3$ and $Cr(OH)_3$, the last two by hydrolysis. MnS undergoes partial oxidation, resulting in a mixture of somewhat indefinite composition consisting of MnS, $MnO(OH)_2$ and Mn_2O_3.

From the color of the solution before precipitation and the color of the group precipitate, draw inferences as to the presence and absence of certain members.

Separation of NiS and CoS. Transfer the washed group precipitate to a beaker or evaporating dish and treat it with 50 ml. of 1:9 HCl (1 part of concentrated HCl to 9 parts of water), stir and allow to settle. *Do not heat.* HCl of this strength will quickly dissolve all except NiS and CoS. The rate of dissolving of NiS and CoS is sufficiently slow to make the separation complete enough for practical purposes.

Filter off the residue and begin the evaporation of the filtrate, in a large evaporating dish, for the detection of other members of this group. The residue may consist of NiS, CoS or dark-colored, gummy sulfur. Make a preliminary test for nickel and cobalt with a borax bead. A blue bead shows cobalt, a reddish brown bead shows nickel. Since small amounts of cobalt may not be detected when present with large amounts of nickel in the bead, better identifying tests must be made.

Dissolve the residue in a few milliliters of aqua regia and evaporate to a small volume, being careful not to carry the evaporation to dryness. Dilute with a few milliliters of dilute HCl and filter to remove the black sulfur. Add NaOH dropwise until a permanent precipitate forms. Dissolve this in dilute acetic acid, adding a slight excess.

Detection of Nickel. To a small portion of this solution, made slightly ammoniacal with NH_4OH, add 1 ml. of dimethylglyoxime. A heavy red precipitate of nickel dimethylglyoxime shows nickel. This test will verify the borax bead test.

Detection of Cobalt. To another portion of the solution add a little dilute HCl, warm and then add 1 ml. of α-nitroso-β-naphthol reagent. A reddish precipitate of cobalti-nitroso-β-naphthol, $Co(C_{10}H_6NOO)_3$, shows cobalt.

If this reagent is not available use the cobaltinitrite test. This

is carried out as follows: To a portion of the solution, acid with acetic acid, add solid KCl until saturated and then an equal volume of 50 per cent KNO_2 solution. After an hour or more a yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$, will form.

Separation of Manganese and Iron. The filtrate from the separation of NiS and CoS may contain Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}, Zn^{++} and excess HCl. Evaporate the solution to a few milliliters in a large evaporating dish in order to remove excess HCl, dilute to about 100 ml. with water and then make strongly alkaline with an excess of strong NaOH solution. Without filtering add cautiously 2 grams of Na_2O_2 and boil the solution for a few minutes while stirring constantly. Partly neutralize the solution with dilute HNO_3, filter and wash the precipitate, if one forms, with hot water. Reserve the filtrate for tests for aluminum, chromium and zinc.

Detection of Manganese. A brown precipitate may be either $MnO(OH)_2$ or $Fe(OH)_3$ or both. Dissolve a small amount of this brown precipitate in 5 ml. of concentrated HNO_3, adding a few drops of H_2O_2 to hasten the dissolving. To the solution add a small quantity of $NaBiO_3$, shake and allow the suspended solids to settle. A pink supernatant liquid, due to the formation of permanganate ions, shows the presence of manganese.

A bead test will further confirm the presence of manganese. In the loop of a platinum wire fuse some Na_2CO_3, touch it to the brown precipitate, and then dip it into powdered $KClO_3$ and heat. A green or greenish blue bead, due to sodium manganate, Na_2MnO_4, proves the presence of manganese.

Detection of Iron. Take a small portion of the brown precipitate, dissolve it in dilute HCl, boil, cool and add a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$. A heavy blue precipitate, Prussian blue, $Fe_4[Fe(CN)_6]_3$, proves the presence of iron. Avoid an excess of $K_4Fe(CN)_6$ because the precipitate is soluble in an excess of the reagent. A light blue, slight precipitate may be due to mere traces of iron and should not be reported.

An extremely delicate test for traces of iron is the reddish color imparted to ferric solutions by KCNS. This test should not be used here since enough iron is usually present as an impurity in the reagents to give this reaction.

Separation and Detection of Aluminum. The filtrate from the $NaOH\text{-}Na_2O_2$ treatment may contain AlO_2^-, $CrO_4^=$ and $ZnO_2^=$ ions together with excess NaOH. Neutralize the alkali with dilute

HNO_3, add a little NH_4Cl to prevent the precipitation of $Zn(OH)_2$ and then render the solution slightly ammoniacal with NH_4OH. The solution should have only faint odor of ammonia; too large an excess renders the $Al(OH)_3$ appreciably soluble; boil to remove the excess if too much has been added. Filter.

If a white precipitate forms, aluminum is probably present. Remove most of the gelatinous precipitate to a test tube, dissolve it with dilute HCl, add 3 ml. of ammonium acetate solution and 5 ml. of " Aluminon " reagent. Mix thoroughly and then make the solution alkaline with dilute NH_4OH. The bright red color of the precipitated $Al(OH)_3$ identifies aluminum.

The formation of Thenard's blue as a test for aluminum may also be carried out. Proceed as follows: Tear off a portion of the filter paper which is coated with the precipitate, hold it in the loop of a platinum wire, moisten with a few drops of dilute $Co(NO_3)_2$ and ignite. A blue color in the charred paper, due to a double oxide, $CoO \cdot Al_2O_3$, known as Thenard's blue, shows the presence of aluminum. If the $Co(NO_3)_2$ solution is too strong black cobalt oxide may result.

Silicic acid, H_2SiO_3, resembles $Al(OH)_3$ in appearance. It is derived from the glass vessels and may precipitate at this point. It may be distinguished from $Al(OH)_3$ by evaporating the solution to dryness and then treating the residue with HCl which, if it is SiO_2, will remain insoluble.

Detection of Chromium. The filtrate from the $Al(OH)_3$ separation may contain $CrO_4^{=}$ and $Zn(NH_3)_4^{++}$ ions. Acidify the solution with dilute $HC_2H_3O_2$, add 1 gram of $NaC_2H_3O_2$, heat to boiling and while hot add dropwise $BaCl_2$ reagent. If a yellow precipitate forms allow it to settle and then filter through two thicknesses of filter paper. Set aside the filtrate for the detection of zinc.

Dissolve the $BaCrO_4$ on the filter paper in dilute HNO_3, using warm acid if necessary. Add the filtrate to a test tube containing 1 ml. of ether and 1 ml. of 3 per cent H_2O_2. If chromium is present the ether layer will be blue. The blue color is due to a perchromic acid of indefinite composition, and becomes very pronounced in the ether layer.

Detection of Zinc. Zinc in the form of ionized $Zn(C_2H_3O_2)_2$ may be present in the filtrate from the $BaCrO_4$ separation. Pass H_2S into this filtrate. A white precipitate is ZnS and shows the pres-

ence of zinc. If the precipitate is dark colored, indicating traces of FeS, NiS or CoS, add a little HCl, filter and then add Na_2O_2 to the filtrate. Filter off and discard the precipitate which forms. ZnS can then be precipitated from the filtrate.

Zinc can best be identified by means of the dye, Orange IV, as described on page 190. Proceed as follows: Dissolve a portion of the ZnS precipitate in dilute H_2SO_4. To a drop of the dyestuff reagent on a watch glass or spot plate, add a drop of dilute 1:24 H_2SO_4 and then 3 to 5 drops of freshly prepared $K_3Fe(CN)_6$ solution. This will produce a red color. Then add a drop of two of the zinc solution; the green color shows the presence of zinc.

ZnS can be further identified by a test similar to that for aluminum. Coat a portion of the filter paper with the white precipitate, moisten with $Co(NO_3)_2$, hold in a platinum wire and strongly ignite. A green color on the charred paper, a mixture of CoO and ZnO, proves the presence of zinc. Specially prepared test paper may also be used here.

Procedure — Presence of Interfering Anions

Oxalates interfere with the analysis of the cations because CaC_2O_4, SrC_2O_4 and BaC_2O_4 are insoluble in an ammoniacal solution. Consequently, if any of these alkaline earth elements are present, together with oxalate ions, when the solution is made ammoniacal in Group III, the oxalates of calcium, barium and strontium will be precipitated along with the sulfides and hydroxides of Group III and subsequently will not be found in Group IV. It therefore becomes necessary to test for oxalates and, if present, to remove them before the analysis of Group III is begun.

Tartrates and certain types of **organic materials** like sugar and starch interfere with Group III analysis because they hinder the precipitation of $Al(OH)_3$ and $Cr(OH)_3$. They, too, must be tested for and removed before the analysis of Group III is begun.

Phosphates interfere with the cation analysis because the phosphates of the alkaline earths, which are insoluble in basic or neutral solutions, will be precipitated along with Group III when the solution is made ammoniacal during the addition of Group III reagent, and consequently calcium, barium and strontium as well as magnesium will not be found in their regular places in Group IV and Group V.

Phosphates must therefore be tested for before Group III analysis is begun and the usual scheme modified to overcome their interference.

Procedure in the Presence of Oxalates and Tartrates

Test for oxalates as follows: Boil a small portion of the filtrate from Group II to expel H_2S and add an excess of Na_2CO_3. Filter if necessary. Make the filtrate slightly acid with acetic acid, boil and then add an equal volume of saturated $CaSO_4$ solution. If oxalates are present a white precipitate of CaC_2O_4 will form.

Test for tartrates, sugar and similar organic material by heating a small portion of the dry sample with concentrated H_2SO_4. A charring or blackening of the residue and the odor of burnt sugar show the presence of organic material.

If the tests show the presence of these substances, evaporate the filtrate from Group II to dryness, add 5 ml. of concentrated H_2SO_4 and heat until the mass chars. Then add 5 ml. of concentrated HNO_3 and heat until SO_3 fumes are evolved. Repeat the nitric acid treatment until the resulting solution is practically

DIAGRAMMATIC SCHEME — OXALATE AND TARTRATE SEPARATION

Solution:		*Residue:*		*Filtrate:*	
Filtrate from Group II may contain Group III, Group IV, Group V, and $C_2O_4^{=}$, $C_4H_4O_6^{=}$, etc.	Test for $C_2O_4^{=}$ and $C_4H_4O_6^{=}$ in separate portions. Evaporate to dryness, add 5 ml. concentrated H_2SO_4; heat; add 5 ml. concentrated HNO_3, heat until solution clears up. Dilute and filter.	$Cr_2(SO_4)_3$ $BaSO_4$ $SrSO_4$ $CaSO_4$	Boil with Na_2CO_3, filter. Dissolve residue in HCl.	Cr^{+++}	Test for Cr^{+++} if filtrate is green.
				Residue: Ba^{++} Sr^{++} Ca^{++}	Analyze according to Group IV procedure.
		Filtrate: Group III Group V	Analyze for cations according to regular procedures for Groups III and V.		

clear. During this treatment $BaSO_4$, $SrSO_4$, $CaSO_4$ and possibly $Cr_2(SO_4)_3$ will be formed as an insoluble residue. Cool the solution, dilute with water and filter. The filtrate will be Group III and Group V and the residue will consist of the sulfates of Group IV.

Analyze the filtrate for members of Group III, according to the regular procedure already given under the Ammonium Sulfide Group (page 304), and pass on to Group V (page 313).

Boil the residue with 5 grams of Na_2CO_3 in 25 ml. of water, filter, wash the residue and dissolve it with dilute HCl. Analyze the filtrate for chromium (if green) and for barium, calcium and strontium according to the procedure for the Ammonium Carbonate Group, page 312.

Procedure in the Presence of Phosphates

The removal of phosphates is based on the fact that in weak acetic acid, $FePO_4$, $AlPO_4$ and $CrPO_4$ are insoluble, whereas $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ are soluble. If, therefore, the phosphate ions are precipitated with the trivalent ions, Al^{+++}, Cr^{+++} and Fe^{+++}, the alkaline earth cations will remain in the filtrate and can be detected in their regular places in Group IV. The quantity of phosphate present in the sample may be in excess of the trivalent metals present; therefore in order to insure complete precipitation of the phosphate, Fe^{+++} ions in the form of $FeCl_3$ are added in excess.

The detailed procedure is as follows: Test for phosphates by taking a few milliliters of the filtrate from Group II; boil to remove H_2S, add a few drops of concentrated HNO_3, evaporate nearly to dryness, take up with 5 ml. of dilute HNO_3, warm and add ammonium molybdate. If phosphates are present a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$, will form.

If phosphates are thus shown to be present, the next step is to test for ferric iron. Treat a few milliliters of the filtrate from Group II with a few drops of concentrated HNO_3 to oxidize the iron to the ferric state and then add a few drops of $K_4Fe(CN)_6$. A blue precipitate of Prussian blue, $Fe_4[Fe(CN)_6]_3$, shows the presence of iron. This test for iron is necessary at this point because $FeCl_3$ is later added to precipitate completely the phosphate.

Boil the filtrate from Group II to remove H_2S, make it just ammoniacal with NH_4OH and then add, dropwise, enough dilute HCl to make the solution slightly acid. Add 7 to 8 grams of $NH_4C_2H_3O_2$ and 10 ml. of 50 per cent $HC_2H_3O_2$. If sufficient iron is present to precipitate all of the phosphate as $FePO_4$ and still leave the solution red, there will be an excess; otherwise add enough $FeCl_3$ solution, dropwise, until the solution turns red. The red color is due to $Fe(C_2H_3O_2)_3$. Dilute the solution to about 100 ml. and heat to boiling. The boiling will precipitate the excess iron as basic ferric acetate, $Fe(OH)_2C_2H_3O_2$.

The precipitate may consist of $FePO_4$, $AlPO_4$, $CrPO_4$, and $Fe(OH)_2C_2H_3O_2$ and all the phosphate will have been removed from solution.

Analyze the filtrate for Groups III, IV and V according to the schemes given under cation analysis, omitting the tests for Al, Cr and Fe which are now in the precipitate obtained above. Test

DIAGRAMMATIC SCHEME — PHOSPHATE SEPARATION

Solution:		*Precipitate:*		*Precipitate:*	
Filtrate from Group II may contain $Po_4^{\equiv}$, Fe^{+++}, Al^{+++}, Cr^{+++}. Other members of Group III Ba^{++}, Sr^{++}, Ca^{++}, and Group V.	Test for $PO_4^{\equiv}$ and Fe^{+++} in separate portions. Add NH_4OH, then HCl till *just* acid. Add $NH_4C_2H_3O_2$, $HC_2H_3O_2$ and $FeCl_3$ until red; boil.	$FePO_4$ $Fe(OH)_2C_2H_3O_2$ $AlPO_4$ $CrPO_4$	Add water, Na_2O_2; boil.	$Fe(OH)_3$ *Filtrate:* $AlO_2^{=}$ $CrO_4^{=}$	Analyze by Group III procedure.
		Filtrate: Other members of Group III	Analyze by Group III procedure.		
		Ba^{++} Sr^{++} Ca^{++}	Analyze by Group IV procedure.		
		Group V	Analyze by Group V procedure.		

for Al and Cr by adding water and a little Na_2O_2 to the precipitate, boil, filter off $Fe(OH)_3$ and test the filtrate for aluminum and chromium by the usual methods.

Analysis of Group IV

Group Precipitation. To the filtrate from Group III or 25 ml. of the test solution sample, add NH_4OH until slightly ammoniacal, heat almost to boiling and then add a small amount of $(NH_4)_2CO_3$ reagent. If a precipitate forms, this group is present and in this case continue the addition of the reagent until precipitation is complete; otherwise pass on to Group V. The precipitate may contain $BaCO_3$, $SrCO_3$ or $CaCO_3$ or possibly mixtures of these three substances.

Allow the precipitate to settle, filter it off and wash with hot water. Reserve the filtrate for the detection of magnesium, potassium and sodium. Dissolve the precipitate on the filter with hot, dilute $HC_2H_3O_2$, using several 3-ml. portions of the solvent.

Detection of Barium. Dilute the acetate solution to 50 ml. Take a few milliliters of this and make a preliminary test for barium by adding a few drops of K_2CrO_4 reagent. A yellow precipitate of $BaCrO_4$ indicates the presence of barium.

If barium is thus shown to be present heat the remainder of the solution to boiling and add $NaC_2H_3O_2$ and then K_2CrO_4 reagent until the solution turns yellow, showing that an excess of precipitating agent is present. Allow the precipitate of $BaCrO_4$ to settle, decant the supernatant solution through a filter and finally transfer the precipitate to the filter, washing with hot water. Reserve the filtrate for the tests for strontium and calcium.

This separation of barium from strontium and calcium is not sharp because, if strontium is present and its concentration is very high, some yellow $SrCrO_4$ may precipitate. Since $SrCrO_4$ may be mistaken for $BaCrO_4$ the presence of barium must be confirmed by the flame test.

Dissolve the $BaCrO_4$ on the filter with strong HCl and boil the resulting solution until reduction of the chromate to chromic ion is complete as shown by the green color imparted to the solution. Test for barium by dipping a platinum wire into the solution and then holding it in the flame. A Fisher or Meker burner is better for this test because it gives a hotter flame than a Bunsen burner. A green color in the flame confirms the presence of barium.

If barium is absent omit the next step and proceed with the preliminary test for strontium.

Reprecipitation of Calcium and Strontium. To the filtrate from the $BaCrO_4$ separation, add NaOH until alkaline, heat and then add Na_2CO_3. A precipitate indicates the presence of strontium or calcium, or both. This reprecipitation gets rid of the excess of chromate ions. Filter off the reprecipitated $CaCO_3$ and $SrCO_3$, washing until the filtrate is no longer yellow, discard the filtrate and dissolve the precipitates in hot, dilute acetic acid and dilute to 50 ml. with water.

Preliminary Test for Strontium. To a small portion of the acetate solution, add 1 ml. of a saturated solution of $CaSO_4$, heat and allow to stand for several minutes. If a precipitate forms or the solution becomes turbid, strontium is present.

Saturated $CaSO_4$ solution is used here because the concentration of $SO_4^{=}$ ions is low and Ca^{++} ions will not precipitate in such a solution. If this test shows the absence of strontium, omit the next step.

Detection of Strontium. In the presence of strontium, add to the main portion of the acetate solution 5 ml. of $(NH_4)_2SO_4$ solution, warm, allow to stand a few minutes and then filter.

The precipitate may not be pure $SrSO_4$. Any barium which failed to be precipitated as $BaCrO_4$ will appear here as $BaSO_4$. With high concentrations of calcium, $CaSO_4$ may also be precipitated. The presence of strontium is confirmed by the flame test, the color for strontium being deep red. This test is best made by moistening the precipitate with HCl, and picking up some of the solid with the platinum wire and heating it in the flame.

Detection of Calcium. To the filtrate from the strontium separation, add some ammonium oxalate, $(NH_4)_2C_2O_4$, solution. A white precipitate will be due to CaC_2O_4. This precipitate shows the presence of calcium.

Filter off the precipitate and pour acetic acid through the filter. If it is CaC_2O_4, it will not dissolve.

Confirm the presence of calcium by the flame test. Calcium, if present, will color the flame a yellowish red.

Analysis of Group V

The solution may be the filtrate from Group IV or it may be an unknown on this group only. In either case, use separate portions for the tests for magnesium, potassium and sodium.

Detection of Magnesium. To a separate small portion, about 10 ml., of the solution add a few drops of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to remove traces of the alkaline earth ions which failed to be precipitated in Group IV. Filter and discard the precipitate. Evaporate the filtrate to about 5 ml., filtering off any solid NH_4Cl which may separate, add NH_4OH until ammoniacal and then 2 ml. of Na_2HPO_4. A white crystalline precipitate of $MgNH_4PO_4$ will settle out after standing several minutes if magnesium is present. To confirm the precipitate as $MgNH_4PO_4$, dissolve it in dilute $HC_2H_3O_2$ and render the filtrate ammoniacal; $MgNH_4PO_4$ will be reprecipitated.

To confirm the presence of magnesium, take another portion of the solution, neutralize it if necessary, and add 1 ml. of the para-nitrobenzene-azo-resorcinol test reagent. A deep blue color confirms the presence of magnesium.

Detection of Potassium. To another portion of the sample or the filtrate from Group IV, add about 5 ml. of concentrated HNO_3 and evaporate to small bulk in a large evaporating dish. Transfer the concentrated solution to a smaller dish and evaporate to dryness. Ignite the residue below a dull red heat until fumes are no longer given off. This procedure is necessary in order to decompose and volatilize ammonium salts.

Take up some of the residue with a few milliliters of water, slightly acidified with acetic acid, and filter. To the filtrate add 1 ml. of $Na_3Co(NO_2)_6$, warm and allow to stand. Yellow $K_2NaCo(NO_2)_6$ will precipitate if potassium is present.

Test a small portion of the baked residue by the flame test; a violet-colored flame indicates potassium. If the flame is yellow, view it through a thick cobalt glass; a violet color observed through the glass shows the presence of potassium.

Detection of Sodium. To a drop or two of the test mixture, add 8 to 12 drops of zinc uranyl acetate reagent. In the course of 5 minutes or so, the triple salt, $NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3(UO_2)_2C_2H_3O_2 \cdot 6H_2O$, sodium zinc uranyl acetate will form as a pale yellow precipitate.

A yellow-colored flame obtained in the flame test for potassium is due to sodium. If the flame is a brilliant yellow and persists for some time sodium in appreciable quantities is present. A dull yellow which quickly fades out is due to traces of sodium and should not be reported.

Detection of Ammonium. The test for the NH_4^+ ion must be made on samples before ammonium salts are added as reagents. To a portion of the sample in a small beaker add a strong solution of NaOH. Cover the beaker with a watch glass to the bottom of which is attached a piece of moist, red litmus paper. Warm the mixture. Be careful that no liquid splashes up and touches the test paper. If the test paper turns blue and the odor of ammonia can be detected, ammonium salts are present.

Systematic Analysis of the Acid-Insoluble Residue

Note: For the analysis of the insoluble residue from samples of a more complex nature, which may contain a greater variety of insoluble constituents than likely to be found in the samples of the simple type under consideration, the analyst is referred to the methods given under the analysis of minerals, ores and technical products, page 318.

Treatment of solid unknowns of the type under consideration with acids to get the sample into solution may leave a solid insoluble even in aqua regia. Such insoluble compounds may have been a part of the original mixture or may have been produced by interaction of dissolved constituents or by reaction with the acids used as solvents. An inspection of the solubility table shows that comparatively few substances resist the action of hot concentrated HNO_3. The list includes $BaSO_4$, $SrSO_4$, ($CaSO_4$), $PbSO_4$; the halides of silver and possibly lead and mercurous mercury; the sulfides of mercury; the cyanogen compounds of silver and certain other metals; gelatinous silicic acid from decomposable silicates; oxides of tin and antimony. Free sulfur may result from the action of nitric acid on sulfides and black specks of carbon may be derived from organic matter.

The action of aqua regia, following that of nitric acid, will dissolve the oxides of antimony and tin, Hg_2S and HgS, and transpose, at least partially, the silver halides and complex cyanogen salts into AgCl.

The residue may then consist of the following substances:

$PbSO_4$, ($PbCl_2$)
AgCl, (AgBr, AgI, AgCN, AgCNS, $Ag_3Fe(CN)_6$, $Ag_4Fe(CN)_6$)
$BaSO_4$, $SrSO_4$, ($CaSO_4$)
H_2SiO_3, (SiO_2, silicates)
Sulfur, carbon

Proceed with the systematic analysis of this residue as follows:

1. Digest a portion of residue with hot $NH_4C_2H_3O_2$ solution to dissolve any $PbCl_2$ and $PbSO_4$ which may be present. Examine the filtrate for Pb^{++}, Cl^- and $SO_4^=$ ions.

2. Treat a portion of the residue with NH_4OH. This will dissolve AgCl and some AgBr, and silver can thus be tested for in the filtrate by acidifying it with HNO_3.

3. Roast a portion of the residue in an open dish if particles of black carbon or yellow sulfur are visible. These will be oxidized and removed as CO_2 and SO_2.

4. Mix the roasted residue with 10 times its weight of an equal mixture of Na_2CO_3 and K_2CO_3 in a porcelain crucible and heat over a blast lamp or Meker burner until the fused mass becomes a clear melt. Place the cool crucible in a beaker, cover with water, and boil. Crush the residue with a stirring rod. Filter and wash the residue. Test for sulfates in the filtrate by acidifying with HCl and adding $BaCl_2$; a white precipitate of $BaSO_4$ proves the presence of SO_4. Dissolve a portion of the washed residue with dilute HCl and test for the alkaline earth ions in the resulting solution. Add HNO_3 to another portion of the residue, if dark colored, to dissolve metallic silver and test for silver in the filtrate.

5. Test a portion of the dry residue for SiO_2 by the metaphosphate bead test.

SYSTEMATIC ANALYSIS OF ALLOYS

The alloys given out for analysis are brasses, bronzes, solders, bearing metals, type metals and steels. Alloys are classified as ferrous or non-ferrous according to whether they consist mainly of iron or a mixture of other metals; i.e., the various kinds of iron and steels are ferrous alloys whereas other metals predominate in non-ferrous alloys. Common carbon steels contain, besides iron, fractional percentages of carbon, phosphorus, silicon, sulfur and manganese. Alloy steels may contain, in addition to these elements, small percentages of chromium, nickel, tungsten, vanadium, molybdenum or other metals. The composition of some common non-ferrous alloys is given in Table XV, with the chief constituents in the order of their predominance.

In the systematic analysis of alloys, the metals of Groups I, II and III as well as magnesium should be looked for. Among the

anions only sulfides and sulfates, phosphates and arsenates and silica need be tested for.

TABLE XV

COMPOSITION OF ALLOYS

Bronzes	Cu, Sn, Zn, Pb
Brasses	Cu, Zn, Sn, Pb
Solders	Bi, Sn, Pb
Solders	Zn, Cu, Sn
Auto bearing metals	Sn, Sb, Cu
Pewter	Sn, Sb, Cu, Pb, Zn
Type metals	Pb, Sb, Sn
German silver	Cu, Zn, Ni

Procedure for Dissolving the Alloy. Take about a half-gram of the sample in the form of turnings, drillings or chips and treat with about 10 ml. of dilute HNO_3. Heat until brown fumes are no longer given off. Add more acid if more appears necessary to dissolve the sample. In general, HNO_3 is a better solvent for most metals and alloys than HCl. HNO_3 will oxidize sulfides to H_2SO_4, phosphides to H_3PO_4 and arsenic to H_3AsO_4. Compounds of silicon will become silicic acid and will precipitate as gelatinous H_2SiO_3. Tin, antimony and possibly bismuth will be precipitated as metastannic acid, H_2SnO_3, antimony oxide, Sb_2O_5, and possibly Bi_2O_3. Carbon will remain as black specks of graphite. Some metals like iron, aluminum and chromium become " passive " in strong HNO_3 and dissolve very slowly.

If a white precipitate forms on treatment with HNO_3, indicating tin or antimony, or if the sample appears to be unchanged by HNO_3, decant the solution, saving it for analysis, and replace the HNO_3 by moderately strong HCl, heating the solution almost to boiling. If this fails to effect complete solution of the metallic portions, use aqua regia. Dilute and filter. Combine the filtrates. If silver or lead is present in the alloy the addition of HCl will precipitate AgCl and $PbCl_2$. The compounds of tin, antimony and bismuth will dissolve in HCl.

Analysis of the Combined Filtrate for Cations. Take a 25-ml. portion of the combined filtrate, evaporate it to dryness in a small evaporating dish and heat the residue until it becomes powdery. Take it up with a few milliliters of dilute HNO_3, dilute to 25 milliliters and filter if necessary. Use this filtrate for the analysis of the

cations, remembering that if HCl or aqua regia was used as the solvent for the alloy, Group I cations will have been precipitated. Follow the procedures as given, omitting the tests for the alkaline earths and the alkali metals. If phosphides are likely to be present follow the modification for the removal of phosphates to avoid difficulty in testing for magnesium.

Analysis of the Insoluble Residue. The residue may consist of SiO_2 or H_2SiO_3, $PbCl_2$, AgCl, specks of black carbon or yellowish sulfur or traces of undissolved metals. Test a portion of the residue for silicates by the metaphosphate bead test. Examine another portion for lead and silver by the regular method for these elements.

Analysis for Anions. In a small portion of the combined filtrate, test for sulfates by first neutralizing with NH_4OH, acidifying with HCl and adding $BaCl_2$ solution. A white precipitate of $BaSO_4$ indicates the original presence of sulfides in the alloy, the sulfide having been oxidized to sulfate by the nitric acid used in dissolving the sample.

Phosphides may have originally been present and been oxidized to phosphates. The test for phosphates should therefore be made on the filtrate from cation Group II, using the $(NH_4)_2MoO_4$ test.

SYSTEMATIC ANALYSIS OF ORES, MINERALS AND TECHNICAL PRODUCTS

The samples provided for this analysis may be natural substances such as minerals or ores, or they may be industrial products such as glass, refractories and slags. This exercise is intended primarily to give practice in getting samples of this nature into solution, involving a pyrosulfate fusion in addition to a carbonate fusion.

Use about 1 gram of the finely ground sample. Add 5 ml. of concentrated HNO_3 and warm until the action becomes slow and brown fumes no longer come off. Decant the solution and add another 5 ml. of HNO_3 to the residue. Heat, dilute and filter, combining the filtrate with the decanted solution.

If a residue remains, try to dissolve it in aqua regia, diluting and filtering when action appears to be complete and combining the filtrate with the above solution.

Take the residue insoluble in the above acids, dry and mix with it about 5 grams of potassium bisulfate, $KHSO_4$. Place the mix-

ture in a porcelain crucible and heat over a blast lamp or large Meker burner until a clear fusion results. Allow the crucible to cool and then place it in a beaker and add water. Loosen the fused mass from the crucible and crush the lumps with a glass rod. Add dilute HCl then filter.

The $KHSO_4$ decomposes first into $K_2S_2O_7$ and H_2O and at higher temperatures in SO_3 and K_2SO_4:

$$2KHSO_4 = K_2S_2O_7 + H_2O$$

$$K_2S_2O_7 = K_2SO_4 + SO_3$$

Insoluble materials are acted upon by the $K_2S_2O_7$, converting them into more easily soluble compounds and causing silicates to be more easily decomposed by acids or subsequent fusion. Alkaline earth metals, lead and silver are changed into $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$ and Ag_2SO_4.

Unite the filtrate from this fusion with that obtained by the previous action with acids and analyze by the systematic procedure for cations.

The residue remaining after this fusion, which may consist of the insoluble sulfates, silicates and unattacked portions of the sample, must be fused with Na_2CO_3 to which a small amount of KNO_3 is added. The procedure is like that described previously under "Acid-Insoluble Residue," page 315. A platinum crucible is best for this fusion (provided metals like Pb, Ag, As and Sn are absent), because porcelain crucibles are attacked by fused Na_2CO_3 and contaminate the sample with silica, calcium and aluminum.

SPECIAL ANALYSIS OF SILICATES

The abundance of silicates in minerals, rocks, clays and soils, as gangue in ores and as constituents of many artificial products, makes their analysis important enough to devote a section to their special consideration.

Only the alkali silicates are soluble in water. Some silicates are decomposed by acids, rendering the silicate ion insoluble as gelatinous silicic acid, H_2SiO_3 or $SiO_2{\cdot}xH_2O$, where the silica can be tested for by the metaphosphate bead test, and dissolving the metal constituents as chlorides or nitrates where they can be detected by the usual methods of cation analysis. Most silicates, however,

are not acted upon by mineral acids and require either a fusion or a treatment with hydrofluoric acid to render them soluble.

Procedures for Silicate Analysis

Take a 0.5-gram portion of the finely ground sample, mix it with 5 grams of equal parts of Na_2CO_3 and K_2CO_3 and a half-gram of KNO_3 and place the mixture in a platinum crucible, unless easily reducible metals such as Sn, Sb, Bi, Ag and Pb are likely to be present, in which case a nickel or a porcelain crucible must be used. Heat the crucible over a blast lamp until the melt is clear and ceases bubbling. This action will convert the silicate into soluble sodium silicate and the metals into carbonates, oxides or other forms.

Cool the crucible, place it in an evaporating dish and cover with dilute HCl. Remove the crucible, crush any lumps that may be present and evaporate the solution to dryness. Bake the residue to dehydrate the silicic acid, extract with hot HCl, dilute and filter off the SiO_2. Examine the residue by the metaphosphate bead test and test the filtrate for cations by the usual procedure.

Alternate Method. Take a 0.5 sample, place it in a platinum crucible, add 10 ml. of HF acid and a few milliliters of concentrated H_2SO_4 and warm *in the hood.* Evaporate until dense white fumes of SO_3 appear. This treatment will decompose any silicate, evolving the silicon as SiF_4 and leaving the metals as sulfates. Extract with water, filter if necessary, and examine the filtrate for cations and the residue for such metals as barium, strontium and calcium.

Of special interest in the analysis of silicates is the detection of potassium in minerals such as feldspar, because by geological weathering processes this potash became available as a valuable plant food. Potassium may be detected in the filtrate from the hydrofluoric acid treatment, but a better method is to apply a special fusion. This is known as the J. Lawrence Smith method and is carried out as follows:

Mix a half-gram portion of the finely ground feldspar with an equal weight of NH_4Cl (alkali free) and about 5 grams of pure $CaCO_3$. Place the mixture in a high, covered, platinum crucible and heat to a dull redness for at least half an hour. The action may be shown approximately by the equation:

$$2KAlSi_3O_8 + 6CaCO_3 + 2NH_4Cl = 2KCl + 6CaSiO_3 + Al_2O_3 + H_2O + 2NH_3 + 6CO_2$$

although the effective fusion agent above is doubtless $CaCl_2$ which is formed by the interaction of NH_4Cl with $CaCO_2$.

Allow the crucible to cool, transfer it to an evaporating dish, boil, filter, remove the excess calcium with $(NH_4)_2CO_3$ and examine the final filtrate for potassium.

APPENDIX

REAGENTS

(A) LIQUID REAGENTS

Acetic Acid, $HC_2H_3O_2$, Dilute. Dilute 12.5 ml. of glacial acetic acid to 100 ml. with water.

Alcohol, Ethyl, C_2H_5OH, 95 per cent. (Test reagent for acetates.)

Aluminon, $C_{19}H_9O_2(COONH_4)_3$, the ammonium salt of aurin-tri-carboxylic acid. A 0.1 per cent solution of the dye in water. (Test reagent for aluminum.)

Ammoniacal Silver Nitrate (Miller's Reagent). Dissolve 1.7 grams of $AgNO_3$, 25.3 grams of KNO_3, and 17 ml. of concentrated NH_4OH in water and dilute to 1 liter.

Ammonium Acetate, $NH_4C_2H_3O_2$. 250 grams per liter.

Ammonium Carbonate, $(NH_4)_2CO_3$. Dissolve 100 grams in a mixture of 100 ml. of concentrated NH_4OH and 500 ml. of water. Dilute to 1 liter.

Ammonium Hydroxide, NH_4OH, Concentrated. The concentrated "ammonia," sp. gr. 0.90, containing 28 per cent NH_3 by weight.

Ammonium Hydroxide, NH_4OH, Dilute. 400 ml. of concentrated NH_4OH diluted to 1 liter.

Ammonium Iodide, NH_4I. 150 grams per liter.

Ammonium Molybdate, $(NH_4)_2MoO_4$. To a mixture of 130 ml. of cold water and 75 ml. of concentrated NH_4OH add 50 grams of MoO_3 and stir until dissolved. Add this slowly with constant stirring to a mixture of 240 ml. of concentrated HNO_3 and 575 ml. of water. Allow to stand for several days and then decant the clear solution. (Test reagent for arsenates and phosphates.)

Ammonium Nitrate, NH_4NO_3. 80 grams per liter.

Ammonium Oxalate, $(NH_4)_2C_2O_4$. 35.0 grams $(NH_4)_2C_2O_4 \cdot H_2O$ per liter.

Ammonium Polysulfide, $(NH_4)_2S_2$. Pass H_2S into 200 ml. of concentrated NH_4OH to which has been added 5 grams of sulfur. Then add 200 ml. of concentrated NH_4OH, dilute to 1 liter and filter if necessary.

Ammonium Sulfate, $(NH_4)_2SO_4$. 130 grams per liter.

Aqua Regia. Mix 1 part of concentrated HNO_3 with 3 parts of concentrated HCl. To be prepared by student when needed.

Barium Acetate, $Ba(C_2H_3O_2)_2$.

Barium Chloride, $BaCl_2$. 120 grams of $BaCl_2 \cdot 2H_2O$ per liter.

Barium Hydroxide, $Ba(OH)_2$. Saturated solution. To be kept in a large bottle provided with syphon tube and soda-lime tube. (Test reagent for carbonates.)

Barium Nitrate, $Ba(NO_3)_2$. Dissolve 65 grams in one liter of water. (Anion Group II reagent.)

Calcium Nitrate, $Ca(NO_3)_2$. Dissolve 236 grams of $Ca(NO_3)_2{\cdot}4H_2O$ in 1 liter of water.

Calcium Sulfate, $CaSO_4$. Saturated solution.

Carbon Tetrachloride, CCl_4.

Chloroplatinic Acid, H_2PtCl_6. 10 per cent solution. To be kept in supply room or dispensed by instructor.

Cobalt Nitrate, $Co(NO_3)_2$. 30 grams of $Co(NO_3)_2{\cdot}6H_2O$ per liter. (Test reagent for aluminum and zinc.)

Dimethylglyoxime (diacetyldioxime), $C_4H_8N_2O_2$. 10 grams dissolved in 1 liter of 95 per cent alcohol. (Test reagent for nickel.)

Ether, Ethyl, $(C_2H_5)_2O$.

Ferric Chloride, $FeCl_3$. 100 grams $FeCl_3{\cdot}6H_2O$ in 990 ml. of water acidified with 10 ml. of concentrated HCl.

Ferrous Sulfate, $FeSO_4$. 250 grams of $FeSO_4{\cdot}7H_2O$ or 392 grams $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ per liter. (Freshly prepared.)

Hydrochloric Acid, HCl, Concentrated. C. P. reagent. 37 per cent HCl by weight; sp. gr., 1.19.

Hydrochloric Acid, HCl, Dilute. Dilute the concentrated reagent with 2 volumes of water.

Hydrogen Peroxide, H_2O_2. 3 per cent commercial solution.

Hydrogen Sulfide, H_2S. May be prepared by the action of commercial HCl on FeS, in individual student generators (see Fales, *Inorganic Quantitative Analysis*, page 20), in Kipp generators or for large sections in larger generators (see Reedy, *Elementary Qualitative Analysis*, pages 131–134). It may also be made by heating a specially prepared mixture of paraffin wax and sulfur, sold under the trade name of "Aitchtuess." The compressed gas may also be purchased in cylinders.

Iodine, I_2. Dissolve 1.27 grams in 1 liter of water.

Magnesia Mixture. Dissolve 100 grams of $MgCl_2{\cdot}6H_2O$ and 100 grams NH_4Cl in water, add 50 ml. of concentrated NH_4OH and dilute to 1 liter.

Mercuric Chloride, $HgCl_2$. 50 grams $HgCl_2$ per liter.

Nitric Acid, HNO_3, Concentrated. C. P. reagent, 70 per cent HNO_3 by weight; sp. gr., 1.42.

Nitric Acid, HNO_3, Dilute. Dilute 1 part of the concentrated reagent with 2 parts of water.

***p*-Nitrobenzene-Azo-Resorcinol, $C_{12}H_9N_3O_4$.** Dissolve 0.01 gram of the substance in 1 liter of 2 *M* NaOH. (Test reagent for magnesium.)

α-Nitroso-β-Naphthol, $C_{10}H_6OH(NO)$. Saturated solution in 50 per cent acetic acid. (Test reagent for cobalt.)

Orange IV. Dissolve 0.01 gram of Tropeolin 00 in 100 ml. of water. (Test reagent for zinc.)

Potassium Chromate, K_2CrO_4. 97 grams per liter.

Potassium Cyanide, KCN. 65 grams per liter.

Potassium Ferricyanide, $K_3Fe(CN)_6$. 100 grams per liter.

Potassium Ferrocyanide, $K_4Fe(CN)_6$. 106 grams per liter.

Potassium Iodide, KI. 166 grams per liter.

Potassium Permanganate, $KMnO_4$. 16 grams per liter.

Potassium Thiocyanate, KCNS. 100 grams per liter.

Rhodamine B. Dissolve 0.01 gram in 100 ml. of water. Reagent to be dispensed by instructor. (Test reagent for antimony.)

Silver Acetates, $AgC_2H_3O_2$. Saturated solution.

Silver Nitrate, $AgNO_3$. 50 grams per liter.

Sodium Acetate, $NaC_2H_3O_2$. 400 grams per liter.

Sodium Carbonate, Na_2CO_3. Molar solution.

Sodium Cobaltinitrite, $Na_3Co(NO_2)_6$. Dissolve 100 grams of $NaNO_2$ in 300 ml. of water, add 10 ml. of acetic acid and 10 grams of $Co(NO_3)_2 \cdot 6H_2O$. Allow to stand a day and filter if necessary. Fresh reagent must be prepared frequently, since it is somewhat unstable.

Sodium Hydrogen Phosphate, Na_2HPO_4. 120 grams $Na_2HPO_4 \cdot 12H_2O$ per liter.

Sodium Hydroxide, NaOH. 4 *M* solution.

Sodium Hypochlorite, NaOCl. Use a solution of bleaching powder.

Sodium Nitroprusside, $Na_2FeNO(CN)_6$. 10 per cent solution.

Sodium Stannite, Na_2SnO_2. To be prepared by student as needed by adding strong NaOH solution to stannous chloride solution (as prepared below) until the precipitate first formed redissolves.

Stannous Chloride, $SnCl_2$. 115 grams of $SnCl_2 \cdot 2H_2O$ in 170 ml. of concentrated HCl and diluted to 1 liter. Add a few pieces of tin foil to prevent oxidation of the reagent.

Starch Solution.

Sulfuric Acid, H_2SO_4, Concentrated. C. P. reagent, 95 per cent; sp. gr., 1.84.

Sulfuric Acid, H_2SO_4, Concentrated. Commercial, impure, for making cleaning mixture.

Sulfuric Acid, H_2SO_4, Dilute. Pour one part of concentrated H_2SO_4 (C.P.) slowly and with constant stirring into 4 parts of water.

Zinc Nitrate, $Zn(NO_3)_2$. Dissolve 149 grams of $Zn(NO_3)_2 \cdot 6H_2O$ and make up to 1 liter. (Anion Group III reagent.)

Zinc Uranyl Acetate. Dissolve 10 grams of uranyl acetate in 6 grams of 30 per cent acetic acid, warming, if necessary, and dilute to 50 ml. In a separate vessel mix 30 grams of zinc acetate with 3 grams of 30 per cent acetic acid and dilute to 50 ml. Mix these two solutions, add a pinch of NaCl, allow to stand 24 hours and then filter. (Test reagent for sodium.)

(B) SOLID REAGENTS

(Used in rather large quantities)

Aluminum (turnings, wire or foil).
Ammonium acetate, $NH_4C_2H_3O_2$.
Ammonium chloride, NH_4Cl.
Ammonium nitrate, NH_4NO_3.
Borax, $Na_2B_4O_7 \cdot 10H_2O$.
Ferrous sulfate, $FeSO_4 \cdot 7H_2O$.
Fusion mixture ($Na_2CO_3 + K_2CO_3$).

Iron nails.
Lead acetate test paper, $Pb(C_2H_3O_2)_2$.
Litmus paper (red and blue).
Magnesium powder.
Paraffin wax.
Potassium acid sulfate, $KHSO_4$.
Potassium chlorate, $KClO_3$.
Potassium nitrite, KNO_2.
Sodium acetate, $NaC_2H_3O_2$.
Sodium bismuthate, $NaBiO_3$.
Sodium carbonate, Na_2CO_3.
Sodium dichromate, $Na_2Cr_2O_7$ (commercial).
Sodium hydroxide, NaOH.
Sodium peroxide, Na_2O_2.
Sodium sulfite, $Na_2SO_3{\cdot}7H_2O$.
Starch.
Starch-iodide paper.
Turmeric paper.
Zinc, granulated C. P.

(C) SUPPLEMENTARY REAGENTS

In addition to the test solutions for cation and anion analysis, and the liquid and solid reagents listed above, all of which must be kept supplied and a reserve carried in stock, it is convenient to provide an additional reagent rack carrying supplementary reagents for which there may be an occasional demand. Among these should be the dry C. P. nitrates (or chlorides) of the metals and the alkali salts of the acid radicals, so that these salts will be accessible to the student whenever desired. Small wide-mouthed bottles of about 100-ml. capacity will serve as containers. Other additional reagents are the following:

Ammonium carbonate, $(NH_4)_2CO_3$.
Ammonium sulfate, $(NH_4)_2SO_4$.
Arsenious oxide, As_2O_3.
Benzol, C_6H_6 (solvent for sulfur).
Calcium fluoride, CaF_2.
Copper (foil, turnings, shot).
Ferric chloride, $FeCl_3$.
Ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$.
Iodine (crystals).
Manganese dioxide, MnO_2.
Oxalic acid, $H_2C_2O_4{\cdot}2H_2O$.
Potassium iodide, KI.
Potassium permanganate, $KMnO_4$.
Potassium chromate, K_2CrO_4.
Rochelle salts.
Sand.
Sugar.
Sulfur (flowers).
Tin foil.

REPRESENTATIVE LIST OF DESK EQUIPMENT

2 evaporating dishes 60 mm.
2 evaporating dishes 145 mm.
2 casseroles 100 ml.
1 graduate 100 ml.
1 graduate 10 ml
2 watch glasses 150 mm.
2 watch glasses 75 mm.
2 watch glasses 30 mm.
1 pipette 10 ml.
1 pipette 50 ml.
8 Erlenmeyer flasks, 2 150-ml., 4 300-ml., 2 500-ml.
1 Florence flask, 500 ml.
8 beakers, 2 200-ml., 4 400-ml., 2 1000-ml.
4 funnels 65 mm.
1 test tube rack.
24 test tubes, 15 cm.
1 test tube brush.
2 Bunsen burners.
2 burner tips.
2 filter stands.
1 iron stand.
2 iron rings with clamps.
1 spatula.
1 Nichrome triangle.
1 mortar and pestle, 125 mm.
1 triangular file.
2 250-ml. bottles.
1 500-ml. W. M. bottle.
2 crucibles.
1 filter flask.
1 test tube holder.
2 wire gauzes.
1 vial red litmus paper.
1 vial blue litmus paper.
1 sponge.
2 towels.
2 lengths rubber tubing.

TEST SOLUTIONS OF CATIONS

Make stock test solutions by dissolving the weight given in the last column in water (or acids when indicated) and dilute to one liter. The stock solutions are of such strength that each milliliter contains 100 milligrams of the metallic ion. For student use and making unknowns dilute the stock solution with 9 times its volume of water.

Cation	Salt	Grams per Liter
Ag^{+}	$AgNO_3$	157
Hg_2^{++}	$Hg_2(NO_3)_2 \cdot 2H_2O$ (*a*)	140
Pb^{++}	$Pb(NO_3)_2$	160
Hg^{++}	$Hg(NO_3)_2$ (*a*) $\frac{1}{2}H_2O$	167
Bi^{+++}	$Bi(NO_3)_3 \cdot 5H_2O$ (*a*)	233
Cu^{++}	$Cu(NO_3)_2 \cdot 6H_2O$	465
Cd^{++}	$Cd(NO_3)_2 \cdot 4H_2O$	278
As^{+++}	As_2O_3 (*b*)	13*
As^{+++++}	As_2O_5	153
Sb^{+++}	$SbCl_3$ (*b*)	188
Sn^{++}	$SnCl_2 \cdot 2H_2O$ (*b*)	188
Sn^{++++}	$SnCl_4 \cdot 5H_2O$	294
Ni^{++}	$Ni(NO_3)_2 \cdot 6H_2O$	500
Co^{++}	$Co(NO_3)_2 \cdot 6H_2O$	500
Mn^{++}	$Mn(NO_3)_2 \cdot 6H_2O$	530
Fe^{+++}	$Fe(NO_3)_3 \cdot 9H_2O$	715
Al^{+++}	$Al(NO_3)_3 \cdot 9H_2O$	1388
Cr^{+++}	$Cr(NO_3)_3 \cdot 9H_2O$	770
Zn^{++}	$Zn(NO_3)_2 \cdot 6H_2O$	455
Ba^{++}	$Ba(NO_3)_2$	190
Sr^{++}	$Sr(NO_3)_2$	240
Ca^{++}	$Ca(NO_3)_2 \cdot 4H_2O$	590
Mg^{++}	$Mg(NO_3)_2 \cdot 6H_2O$	106*
K^{+}	KNO_3	259
Na^{+}	$NaNO_3$	370
NH_4^{+}	NH_4NO_3	445

* Solution 1 ml. = 10 mg. metallic ions; therefore do not dilute.
(*a*) Use dilute HNO_3 to dissolve the salts.
(*b*) Use dilute HCl to dissolve the salts.

TEST SOLUTIONS OF ANIONS

Dissolve the indicated weight of salt in distilled water and make up to one liter. This will give stock test solutions of such strength that each cc. contains 50 milligrams of the non-metallic ion with the exception of the oxalate (*) which directly contains 10 mg. per ml. For student test solutions and making unknowns dilute the stock solution (except oxalate) with 4 times its volume of water.

Anion	Salt	Quantity to Yield 50 Mg. Anion/Ml.
$CO_3^{=}$	Na_2CO_3	88
$C_2O_4^{=}$	$Na_2C_2O_4$	15.2*
F^-	KF	152
BO_2^-	$Na_2B_4O_7 \cdot 10H_2O$	111
$SO_3^{=}$	Na_2SO_3	80
AsO_2^-	$NaAsO_2$	60.7
$AsO_4^{\equiv}$	$Na_2HAsO_4 \cdot 7H_2O$	112.2
$PO_4^{\equiv}$	$Na_2HPO_4 \cdot 12H_2O$	190
$C_4H_4O_6^{=}$	$Na_2C_4H_4O_6 \cdot 2H_2O$	78
$SO_4^{=}$	Na_2SO_4	75
$CrO_4^{=}$	K_2CrO_4	85
$S^{=}$	$Na_2S \cdot 9H_2O$	375
CN^-	NaCN	95
$Fe(CN)_6^{\equiv\equiv}$	$K_4Fe(CN)_6 \cdot 3H_2O$	99.9
$Fe(CN)_4^{\equiv}$	$K_3Fe(CN)_6$	77.6
$S_2O_3^{=}$	$Na_2S_2O_3 \cdot 5H_2O$	111
CNS^-	KCNS	87
I^-	KI	65
Br^-	KBr	75
Cl^-	NaCl	82.5
ClO_3^-	$KClO_3$	73
$C_2H_3O_2^-$	$NaC_2H_3O_2 \cdot 3H_2O$	115
NO_2^-	$NaNO_2$	75
NO_3^-	$NaNO_3$	68.5
$SiO_3^{=}$	$Na_2SiO_3 \cdot 5H_2O$	133

* 10 mg. directly.

SOLUBILITY TABLE

	Ag^+ (1)	Pb^{++} (1)	Hg_2^{++} (1)	Hg^{++}	Bi^{+++} (2)	Cu^{++}	Cd^{++}	As^{+++}	Sb^{+++} (2)	Sn^{++}	Sn^{++++}	Ni^{++}	Co^{++}	Fe^{++}
Nitrite, NO_2^-	Hot W	W	W	W	—	W	W	—	—	—	—	W	W	—
Sulfide, $S^=$	HNO_3	HNO_3	aq. reg.	aq. reg.	HNO_3	HNO_3	HNO_3	HNO_3	strong HCl	strong HCl	strong HCl	HNO_3	HNO_3	HCl
Sulfite, $SO_3^=$	HNO_3	HNO_3	HNO_3	HCl	—	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Thiosulfate, $S_2O_3^=$	HNO_3	HNO_3	—	—	—	—	W	—	—	W	W	W	W	W
Carbonate, $CO_3^=$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	—	—	HCl	HCl	HCl
Arsenite, $AsO_3^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Arsenate, $AsO_4^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	HCl	HCl	HCl	HCl	HCl
Phosphate, $PO_4^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	HCl	HCl	HCl	HCl	HCl	HCl
Chromate, $CrO_4^=$	HNO_3	HNO_3	HNO_3	HCl	HCl	W	HCl	—	—	HCl	—	HCl	HCl	—
Sulfate, $SO_4^=$	Sl. W Ins.	Ins.	Sl. W Ins.	Sl. W	Sl. W	W	W	—	HCl	W	—	W	W	W
Borate, $BO_3^{\equiv}$	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Silicate, $SiO_3^=$ (3)	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	—	—	—	HCl	HCl	HCl
Fluoride, F^-	W	Sl. W HNO_3	W	W	HCl	Sl. W HCl	Sl. W HCl	—	Sl. W HCl	W	W	HCl	HCl	Sl. W HCl
Oxalate, $C_2O_4^=$ (4)	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	HCl	HCl	W	HCl	HCl	HCl
Tartrate, $C_4H_4O_6^=$ (4)	HNO_3	HNO_3	Sl. W HNO_3	HCl	HCl	W	HCl	—	HCl	HCl	W	HCl	W	HCl
Ferricyanide, $Fe(CN)_6^{\equiv}$	Ins.	Ins.	—	Ins.	—	Ins.	Ins.	—	—	Ins.	—	Ins.	Ins.	Ins.
Ferrocyanide, $Fe(CN)_6^{====}$	Ins.	Ins.	—	—	—	Ins.	Ins.	—	—	—	Ins.	Ins.	Ins.	Ins.
Thiocyanate, CNS^-	Ins.	HNO_3	HNO_3	W	—	HNO_3	HCl	—	—	—	W	W	W	W
Cyanide, CN^-	Ins.	HNO_3	—	W	—	HCl	HCl	—	—	—	—	HNO_3	HNO_3	Ins.
Iodide, I^-	Ins.	Sl. W HNO_3	HNO_3	HCl	HCl	Sl. W	W	W	Hyd. W HCl	W	Hyd. W HCl	W	W	W
Bromide, Br^-	Ins.	Ins.	Sl. HNO_3 Ins.	W	Hyd. W HCl	W	W	W	Hyd. W HCl	W	W	W	W	W
Chloride, Cl^-	Ins.	Hot W Ins.	HNO_3	W	Hyd. W HCl	W	W	W	Hyd. W HCl	W	W	W	W	W
Acetate, $C_2H_3O_2^-$	Sl. W	W	W	W	W	W	W	—	—	W	W	W	W	W
Nitrate, NO_3^-	W	W	Sl. W HNO_3	W	Sl. W (HNO_3)	W	W	—	—	—	—	W	W	W
Oxide, ($O^=$)	HNO_3	HNO_3	HNO_3	HCl	HNO_3	HCl	HCl	HCl	HCl	HCl	Sl. HCl Ins.	HCl	HCl	HCl
Hydroxide, OH^-	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	HCl	HCl	Ins.	HCl	HCl	HCl

W = water-soluble (solubility at least 1 gram of the salt in 100 cc. of water);
Sl. W = slightly soluble in water (solubility about 0.1 gram per 100 cc. of water);
Hyd. W = hydrolyzed by water yielding a product not soluble in water;
HCl = soluble in hydrochloric acid;
HNO_3 = soluble in nitric acid;
Aq. reg. = soluble in aqua regia;
Ins. = insoluble in acids taken singly or together;
— = compound either does not exist or the proper solvent has not been determined.

SOLUBILITY TABLE (*Continued*)

	Fe+++	Mn++	Al+++	Cr+++	Zn++	Ba++	Sr++	Ca++	Mg++	NH_4+	K+	Na+	Free Acid (H+)
Nitrite, NO_2^-	W	W	—	—	W	W	W	W	W	W	W	W	(gas)
Sulfide, $S^=$	HCl	HCl	Hyd. W HCl	Hyd. W HCl	HCl	W	W	W	W	W	W	W	(gas)
Sulfite, $SO_3^=$	—	HCl	HCl	—	HCl	HCl	HCl	HCl	W	W	W	W	(gas)
Thiosulfate, $S_2O_3^=$	—	W	W	—	W	HCl	W	W	W	W	W	W	—
Carbonate, $CO_3^=$	—	HCl	—	—	HCl	HCl	HCl	HCl	Sl. W HCl	W	W	W	(gas)
Arsenite, $AsO_3^{\equiv}$	HCl	HCl	—	—	HCl	HCl	HCl	HCl	HCl	W	W	W	—
Arsenate, $AsO_4^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Phosphate, $PO_4^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(liquid)
Chromate, $CrO_4^=$	W	Sl. W HCl	—	HCl	W	HCl Sl. in HNO_3	W	W	W	W	W	W	(solid)
Sulfate, $SO_4^=$	W	W	W	W	W	Ins.	Ins.	Sl. W Ins.	W	W	W	W	(liquid)
Borate, $BO_3^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	Sl. W HCl	Sl. W HCl	HCl	W	W	W	(solid)
Silicate, $SiO_3^=$ (3)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Fluoride, F^-	Sl. W HCl	HCl	W	W	HCl	Sl. W HCl	HCl	Ins.	HCl	W	W	W	(gas)
Oxalate, $C_2O_4^=$ (4)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	W	(solid)
Tartrate, $C_4H_4O_6^=$ (4)	W	Sl. W HCl	W	W	HCl	HCl	HCl	HCl	W	W	W	W	(solid)
Ferricyanide, $Fe(CN)_6^{\equiv}$	W	Ins.	—	—	HCl	W	W	W	W	W	W	W	(solid)
Ferrocyanide, $Fe(CN)_6^{==}$	Ins.	HCl	—	—	Ins.	W	W	W	W	W	W	W	(solid)
Thiocyanate, CNS^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Cyanide, CN^-	—	HCl	—	HCl	HCl	Sl. W HCl	W	W	W	W	W	W	(gas)
Iodide, I^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Bromide, Br^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Chloride, Cl^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Acetate, $C_2H_3O_2^-$	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Nitrate, NO_3^-	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Oxide, $(O^=)$	HCl	HCl	HCl	HCl	HCl	HCl	HCl	Sl. W HCl	HCl	—	W	W	—
Hydroxide, OH^-	HCl	HCl	HCl	HCl	HCl	W	Sl. W HCl	Sl. W HCl	HCl	W	W	W	(liquid)

(1) Addition of HCl will transpose many salts of silver, lead and mercurous mercury into insoluble chlorides.

(2) Many salts of bismuth and antimony show marked hydrolysis with precipitation of water-insoluble products.

(3) The solubility here refers to freshly precipitated and not to native silicates. Decomposition with acids is accompanied by precipitation of gelatinous silicic acid.

(4) Many tartrates and oxalates are soluble in aqueous solutions containing excess tartrate or oxalate ions.

SOLUBILITY OF BASES AND SALTS IN WATER AT 18° C.

	Li	Na	K	Mg	Ca	Sr	Ba	Fe''	Fe'''	Cu''	Zn	Pb	Ag	Hg'	Hg''
F	0.27* 0.1042	4 4 1 048	92 3 15 89—2 aq.	0 0076** 0 0014	0 0016 0 0$_3$205	0 012* 0 0$_3$93	0 163* 0 0093	*			1 6 0 155—4 aq.	0.0641* 0 0026	185 14.32	Decomp.	Decomp.
Cl	77 0 18.16	35 9 6 14	33 4 4 48	54 1 5 68—6 aq.	72 5 6 54—6 aq.	52 8 3 33—6 aq.	35 2 1 69—2 aq.	41 5 3 27—4 aq.	89 8 2 76—12 aq.	75 6 5 62—2 aq.	362 26 54—1½ aq	0.914* 0.0329	0 0$_3$15** 0 0$_4$11	0.0$_3$2** 0.0$_5$43	7.39 0.273
Br	174 0 20.02	89 0 8.65—2 aq.	64 1 5 38	96 1 5 21—6 aq.	141 7 05—6aq.	98 3 96—6 aq.	103 3 46—2 aq	53 5 2 48—6 aq.	s. —6 aq.	v.s. —4 aq.	441 19 59—2 aq.	0.804* 0 0219	0 0$_5$85** 0 0$_6$45	0.0$_5$4** 0 0$_7$7	0.4 0 0111
I	163 0 12.17	176 7 11 79—2 aq.	142 6 8 59	148 5 32—8 aq	203 6 91—6 aq.	176 5 16—6 aq.	195	s.			432 13 55	0 066 0 0014	0 0$_6$3** 0 0$_7$13	0 0$_7$2 0 0$_9$31	**
ClO_3	213.5 23 6	97 0 9 11	6 7 0 546	130 6 80—6 aq.	177.8 8 59—2 aq	175 0 6 88	35 5 1 166—1 aq.	s.	s.	164 7 12—4 aq.	198 8 8.55—4 aq.	151 3 4.05—1 aq.	10? 0.52	**	Decomp.
BrO_3	153 7 11.4	34 0 2.25	6 5 0 389		85 2 87—1 aq.	33 0 95—1 aq.	0 61 0 0155—1 aq.	s.	57 5	s.	58? 1 8—6 aq.	1 34 0 029	0 144* 0 0061	Decomp.	16
IO_3	80 3 4 41	8 5 0 429	7 5 0 350	8 22 0 22—4 aq	0 26* 0 0067—6 aq	0 026* 0 0$_3$60	0.021* 0 0$_3$43—1 aq.	*	*	0 121* 0 0033	0 9* 0 022	0 0019** 0 0$_4$34	0 004** 0 0$_3$14	**	**
NO_3	70 3 10.18—3 aq.	86 0 10.11	29 6 2 93	73 2 4 94—6 aq.	121 2 7 39—4 aq.	67 6 3 20—4 aq.	8 8 0 336	46 5 (24°) 2 58—9 aq.	s.	120 6 40—6 aq.	115 1 6 08—6 aq.	50 7 1.532	204 12 0	Decomp.	v.s.
SO_4	34 3 3.12—1 aq.	16 8 1.182—10 aq.	10 73 0 616	34 6 2 88—7 aq	0 202* 0 015—2 aq	0 0114** 0 0$_3$62	0 0$_3$23** 0 0$_5$99	26 4 1 74—7 aq	*	19 9 1 25—5 aq.	53 0 3 28—7 aq.	0 0041** 0 0$_3$14	0 775 0 0248	0 06 0 0012	Decomp.
CrO_4	110 9 8.54—2 aq.	77.5 4.78—6 aq.	62 8 3 23	72 3 5 15—7 aq	2 34 0 150	0 12* 0 0059	0 0$_3$38** 0 0$_4$15	0 022* 0 0012—2 aq.		**	**	0 0$_4$2** 0 0$_6$62	0 0025** 0 0$_4$75	*	Decomp.
C_2O_4	6.24 (25°) 0.612	3 5 0 261.	37 7 (25°) 2 27—1 aq.	0 03* 0.0027—2 aq.	0 0$_3$56** 0 0$_4$44	0 0045** 0 0$_3$26	0 0089 0 0$_3$40—2 aq.		**	**	0 0$_3$64** 0 0$_4$42—2 aq	0 0$_3$15** 0 0$_5$51	0 0035 0 0$_3$12	**	
CO_3	1.35 0 1823	19 5 1.840—10 aq.	111 5 8 08	0 095* 0 0113—3 aq	0 0013** 0 0$_3$13	0 001** 0 0$_4$68	0 0022** 0 0$_3$11	**	Decomp.	**	0 001** 0 0$_4$81	0 0$_3$11** 0 0$_5$41	0 003** 0 0$_3$11	**	**
$C_2H_3O_2$	v.s. —2 aq.	47 5 73—3 aq.	245 25.0	v.s. —4 aq.	35 0 2 21—2 aq	s.	69 7 2 73—3 aq.	s.	(basic) 0.023* 0 0012	7 2 0 396—1 aq.	40 (25°) 3 21—2 aq.	50 (25°) 1 538—3 aq.	1 005 0 0602	0 75 (13°) 0 029*	
OH	12.8 5.34—1 aq.	107 5 26.9—1 aq.	110 19 6—2 aq.	0 0$_3$84 0 0$_3$15	0 167 0 023	0 78 0 063—8 aq	3 58 0 210—8 aq.	0 0$_3$67 0 0$_4$8	**	**	0 0$_3$56** 0 0$_4$56	0 0155* 0 0$_3$64	0 0022** 0 0$_3$18	**	
PO_4	**	19 6 1.18—12 aq.	v.s.	*	**	**	*	**	**	** —3 aq.	** —4 aq.	**	0 0064** 0 0$_4$13	**	**

The upper number gives the number of grams of solute (calculated as anhydrous) that will dissolve in 100 g. of water at 18° C. The lower number gives the number of moles of solute in 1000 g. of water. If the solid in equilibrium with the saturated solution is a definite hydrate, the symbol aq., preceded by a figure, indicates the number of molecules of water of hydration.

The figures for the solubilities of slightly soluble substances have been abbreviated; thus, 0$_3$15 means 0.00015. A star means a slightly soluble substance—solubility less than about 1 g. in 100 g. of water. A double star means an "insoluble" substance—solubility less than about 0.01 g. in 100 g. of water. s. means soluble; v.s. means very soluble.

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Density of Ammonia Solutions at 15° C.

(According to Lunge and Wiernik)

Specific Gravity	Per Cent NH_3	Specific Gravity	Per Cent NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

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Density of Strong Acids at 15° C. in Vacuo

(According to Lunge, Isler, Naef, and Marchlewsky)

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205	....	33.07	27.95	1.440	74.64	54.07
1.210	....	33.80	28.58	1.445	75.94	54.55
1.215	....	34.53	29.21	1.450	77.24	55.03
1.220	....	35.26	29.84	1.455	78.56	55.50
1.225	....	36.01	30.48	1.460	79.94	55.97
1.230	....	36.76	31.11	1.465	81.38	56.43

DENSITY OF STRONG ACIDS AT 15° C. IN VACUO (*Continued*)

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight HNO_3	Per Cent by Weight H_2SO_4	Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight H_2SO_4	Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight H_2SO_4
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525	....	62.06	1.665	74.24	1.805	87.60
1.530	....	62.53	1.670	74.66	1.810	88.30
1.535	....	63.00	1.675	75.08	1.815	89.16
1.540	....	63.43	1.680	75.50	1.820	90.05
1.545	....	63.85	1.685	75.94	1.825	91.00
1.550	....	64.26	1.690	76.38	1.830	92.10
1.555	....	64.67	1.695	76.76	1.835	93.56
1.560	....	65.20	1.700	77.17	1.840	95.60
1.565	....	65.65	1.705	77.60	1.8405	95.95
1.570	....	66.09	1.710	78.04	1.8410	96.38
1.575	....	66.53	1.715	78.48	1.8415	97.35
1.580	....	66.95	1.720	78.92	1.8410	98.20
1.585	....	67.40	1.725	79.36	1.8405	98.52
1.590	....	67.83	1.730	79.80	1.8400	98.72
1.595	....	68.26	1.735	80.24	1.8395	98.77
1.600	....	68.70	1.740	80.68	1.8390	99.12
1.605	....	69.13	1.745	81.12	1.8385	99.31

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LOGARITHMS

Natural numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

Natural numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

Loga-rithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

Loga-rithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4533	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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INTERNATIONAL ATOMIC WEIGHTS

1943

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	Symbol	*Atomic Number*	*Atomic Weight*		*Symbol*	*Atomic Number*	*Atomic Weight*
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22